NUCLIDE CORPORATION
NUCLIDE ANALYSIS ASSOCIATES
642 EAST COLLEGE AVE., STATE COLLEGE, PENNA.

ANALYSIS OF

THE LUNAR SURFACE AND ATMOSPHERE

BY MASS SPECTROSCOPY

Analysis of The Lunar Surface and Atmosphere by Mass Spectroscopy

Summary Report on

Study Carried out by Nuclide Corporation

642 East College Avenue

State College, Pennsylvania

for

George C. Marshall Space Flight Center

Huntsville, Alabama

Authors:
B. R. F. Kendall
L. F. Herzog
P. J. Wyllie
D. S. Edmonds
C. Bauer

11 January 1964

ANALYSIS OF THE LUNAR SURFACE AND ATMOSPHERE

BY MASS SPECTROSCOPY

ABSTRACT

A study has been made of problems associated with the determination of the composition of the lunar atmosphere and lunar crust by mass spectroscopy.

Methods for determining the mineralogy and petrology of lunar samples from their chemical compositions are summarized. Consideration is given to the characteristics of the lunar environment and its influence on the general design of the lunar instrumentation package. Various types of ion sources, ion mass/charge analyzers and ion detectors are evaluated. Instrument calibration and ground-based data processing are also discussed.

The conclusion of the study is that the most promising type of equipment for the proposed application appears to be a Monopole mass analyzer with an electron bombardment ion source and electron multiplier detector. Vaporization of solid samples would be achieved either by an intense electron beam or by means of an accurately focused laser beam. Automatic calibration checks by intermittently released standard samples of known composition are strongly recommended. A resolving-power multiplier would be used to process telemetered spectra, making it possible to increase the effective resolving power of the lunar analyzer and under suitable conditions to correct for minor instrument aberrations in the event of a hard landing.

Recommendations are made concerning several areas in which further research appears to be justified.

TABLE OF CONTENTS

Chapter 1

INTRODUCTION

ANALYSIS OF THE LUNAR SURFACE AND ATMOSPHERE
BY MASS SPECTROSCOPY

INTRODUCTION

The composition of the surface of the moon is of interest not only to fill an important gap in our knowledge, and because of the clues it can provide on the origin and evolution of the solar system, but also because, within the next few years, we shall be landing manned spacecraft on the moon and later, perhaps, developing military outposts, space-stations, and fuel and material production facilities there.

The lunar gaseous atmosphere (and any particulate "atmosphere" that may be present) is also of interest both for purely scientific reasons and because it is the environment in which men, instruments and machines will have to operate on the moon.

As regards the lunar surface, the engineering aspects perhaps overshadow, for the moment, the intense "purely scientific" interest in Earth's nearest neighbor. Chemical composition is of great importance because, clearly, it will eventually be necessary, for economic reasons, for us to undertake to derive materials from "moon stuff" both to sustain life there and to support exploration missions beyond the Earth-Moon system. The content, distribution and chemical forms (mineralogy) in which water, oxygen, hydrogen, carbon, hydrocarbons, metals, etc., occur are of critical interest in planning for the support of a continuing Manned Space Exploration Program of the Moon and more distant planets.

Determination of the composition of the tenuous lunar gas atmosphere at the very earliest opportunity is essential for a very simple reason: this atmosphere, which in 1960 was a product of the entire life history of the Moon (believed to be about 4,500,000,000 years), and might therefore have given much information on

the evolution of the solar system, has since then been progressively contaminated by materials sent to the Moon from Earth by man, and will soon be irretrievably lost for study. The constituents of the very rarefied (perhaps 10^{-11} torr maximum pressure) original atmosphere will become so extensively mixed with and reacted with propellant and other vapors from spacecraft and rockets that an accurate determination of the composition of the "true" lunar atmosphere will no longer be possible.

Mass spectroscopy offers promise of being able to perform both of these very difficult analytical tasks – and, in addition, of providing isotopic abundance, molecular species, and free-ion concentration data. And it even seems possible that a single device can be designed which can perform both the atmospheric and solid-surface analyses.

In order to provide useful data on partial pressures in the lunar atmosphere, it is believed an instrument must be capable of detecting constituents present at pressures as low as 10^{-13} or even 10^{-14} torr (mm Hg). It should probably also be capable of detecting energetic ions and particles. The instrument need not have a high resolution, but must be built to ultra-high vacuum standards so that it will not contribute significantly itself, by "outgassing", to the spectrum it produces. It must operate successfully in the severe lunar environment.

In the "solids" analysis instrument, high resolution is desirable so that complex molecules may be detected if present; for this purpose also an upper mass range limit approaching 600 is desirable, if feasible. Another important problem that must be solved in any lunar surface analyzer is that of sampling. For a mass spectrometer analyzer, there is the problem of transforming the solid specimen under investigation into free atoms and molecules in an ion source in a reproducible, calibratable fashion, while for all analyzers there is the problem of insuring that the samples analyzed are as representative of the range of lunar surface rock types as possible, or at least of developing criteria whereby the degree of representativeness may be evaluated.

Because the instrument must be taken to the moon by rocket, and because of the character of the lunar environment (with, for example, its large temperature variations, intense primary cosmic rays, and possibly non-negligible concentrations of electrically charged dust), the design of the instrument, especially as regards ion detection and data-processing systems, presents some very special problems. The lunar mass spectroscope must of course be as light as possible, and yet it must be sufficiently rugged to withstand landing shock and thermal shock and retain its alignment. A "trade off" among these conflicting requirements must be made. Means of compensating, through special mass spectrometer output signal analysis techniques, for small misalignments resulting from a less-than-soft landing, should be considered.

It is necessary, too, to consider whether standard samples should be taken along, for analysis after landing, to provide a positive calibration of the apparatus.

Finally, the translation of a chemical analysis into a rock type or mineral assemblage is difficult in the present state of the art. A number of different types of rock may have closely similar major and even minor element contents. An unequivocal decision cannot be made between these if only an accurate bulk chemical analysis is available. It appears, however, that the usefulness of the classical "modal" or "normative" analysis technique of petrology as a specific indicator of lunar rock type can be greatly increased if refined composition-determination experiments of likely lunar rock types are performed terrestrially with a duplicate of the system to be sent to Moon.

The objective of this preliminary study has been to develop criteria by which to judge the suitability of proposed mass spectroscopic systems to the tasks set out in the preceding section, to compile pertinent data on the various kinds of mass spectroscopic analyzers, and therefrom to recommend certain systems that seem to have sufficient promise to warrant construction and further experimental test in the laboratory. At the same time, we have attempted to develop some critical experiments to perform on the moon with the systems selected, in order to determine composition and rock type.

Chapter 2

DETERMINATION OF MINERALOGY AND PETROLOGY OF A SAMPLE ON
THE SURFACE OF THE MOON FROM ITS CHEMICAL ANALYSIS

DETERMINATION OF MINERALOGY AND PETROLOGY OF A SAMPLE
ON THE SURFACE OF THE MOON FROM ITS CHEMICAL ANALYSIS

INTRODUCTION

Since there is as yet no direct evidence available, there are divergent opinions concerning the composition and nature of the lunar surface among the experts on the subject. However, the concensus of opinion is that there is an excellent prospect that the surface rocks of the Moon are chemically identical with terrestrial igneous rocks and/or with meteoritic material. In planning a program for the chemical analysis of lunar samples in situ, therefore, consideration of the compositions of igneous rocks and of meteoritic material which might be encountered is essential. Fortunately, there is a large reservoir of information about the chemistry and mineralogy of igneous rocks and of meteorites to provide a sound basis for such a program. The first direct measurements to be obtained can be at once compared with this collection of data, a procedure which should make possible many deductions which would be unjustified on the basis of the lunar measurements considered alone. Subsequent direct measuring programs would benefit greatly from this dual feed-back—direct feed-back from the first measurements, and feed-back from the reservoir of chemical data.

There are in addition two distinct aspects to the lunar analysis project. The first is the performance of a useful chemical analysis of a lunar sample, and the second is the interpretation of the analysis — the recognition from it of the type of rock from which it comes and the making of such deductions as are permissible on the basis of rock type and chemistry. The amount of petrological and other information extracted from the sample through chemical analysis will depend on the completeness of the analysis, the accuracies of individual measurements, the repre-sentativeness of the sample, and the quality of the data on rocks and meteorites

to which it is compared. One way to approach the problem is to consider four stages:

1. <u>Recognition of rock type</u> is the primary objective. Once rock type has been recognized, the effort involved in the following stages can proceed with enhanced efficiency and can be concentrated on smaller areas of study.

The first important distinction one would attempt to make is that between igneous rock and meteorite; the second would be the recognition of the rock as a member of a specific family of igneous rocks or of meteorites. A possible basis for such distinctions would be the comparison of the concentrations and ratios of certain key elements in the unknown with known compositions of known igneous rocks and meteorites. The known ranges of variability of igneous rock types and meteorites provide indications of the priority which should be given to measurements of specific elements, attention being concentrated initially upon those elements which seem to offer the best prospects for making the necessary distinctions. Attention must also be given to specifying the sensitivities, precisions, and accuracies required if such measurements are to be successful in establishing the required distinctions.

<u>Perhaps as few as two or three element ratios will suffice for this first classification of the rock,</u> as indicated in the following discussion.

A procedure can be worked out most straightforwardly for this part of the program by considering only those types of rock which have been most commonly proposed as lunar materials; these include basaltic rocks, granitic rocks (including acidic ash falls or flows), and chondrites. <u>However, it should be borne in mind that in fact almost any kind of known igneous rock or meteorite might be encountered, and that rocks with no terrestrial equivalents could conceivably occur.</u> It is quite possible, too, that unless placement of the probe on the moon be closely observed and controlled, the sample measured could be taken from an outcrop which is quite

atypical of the average surface material of the moon. The sample, and hence the analysis returned, could, for example, come from a mineralized zone, or from a vein deposit, such as may occur at scattered localities on the surface of the Moon (if there has been igneous activity there), if the instrument package should happen to land on one of these or some other rare outcrop. It is important, therefore, that the instrument selected should be versatile, and not limited in its analysis capabilities to specific narrow analytical paths in the expectation of finding one or the other of a very few "most probable" rock types. The program must, of course, be based on current best evidence and inference as to expected rocks, but flexibility must be maintained in the event the inferences prove to be in error or the probe inadvertently samples an atypical rock.

2. The chemical analysis should, first, provide enough information for the sample to be given a name. Then, the analysis should be examined with the aim of classifying the rock in as detailed a fashion as possible. If the sample proves to be an igneous rock, the minerals quartz, alkali and plagioclase feldspars, pyroxenes, and olivines will be of most significance in classification.

Unfortunately, chemical analysis does not per se provide one with a mineralogy for the rock unequivocally, and rock classification, which is based on mineralogy, therefore cannot be made directly. To overcome this difficulty, the so-called "normative" classification technique would probably be most useful. This recasts a chemical analysis into standard mineral molecules which can then be used as a basis for a mineralogical classification of the rock. For many igneous rocks the "normative" minerals (minerals calculated from chemical content) approximate very closely to the "modal" minerals (the actual mineral content of the rock). This is true for basaltic and granitic rocks, which have been widely proposed as probable rocks on the lunar surface. The calculated norm of the silicate portion of a meteorite is likewise a useful basis for its classification within the family of

meteorites. However, in order to calculate the norm of a rock, it is necessary to know the weight percentages of at least 10 oxides, and 13 or 14 are usually used in such calculations. These include the major elements O, Si, Al, Fe, Mg, Ca, Na, and K, all of which must be measured with high accuracy.

3. The concentrations of certain trace elements may by themselves permit the distinction of one rock type from another. For example: nickel (Ni) is present only in trace amounts in most igneous rocks, but in most meteorites it is present in much greater quantities. This element alone, therefore, might suffice to distinguish between nearly all igneous rocks and meteorites − although obviously, no program should rely upon a single measurement to make this distinction. But data on trace element concentrations in the lunar sample would provide additional evidence to confirm or dispute the conclusions reached on the basis of the major element determination, and, when used in making comparisons between the lunar material and known terrestrial igneous rocks and meteorites, would make possible much finer distinctions as to rock type.

The radioactive elements constitute an important group of trace elements which should also be measured, if possible, since they will provide preliminary information about heat production in lunar material. Other trace elements whose determination is important include those with isotopes which are used in rock age determinations, and those whose isotope ratios give other clues as to origin and history. This group includes at least the elements U, Th, Pb, Rb, Sr, K, Ar, Ca, S, Si, O, C, and H.

4. The proposed program does not end with the recognition and classification of the rock type and with the measurement of specific groups of trace elements. For complete characterization of the rock sample, a complete chemical analysis can provide much additional information. Therefore, the concentrations of as many elements as possible should be measured. An enormous store of analytical

data is now available for terrestrial igneous rocks and for meteorites, and in order to obtain maximum advantage from a single lunar sample, the maximum number of elements and isotopes should be determined for comparison against this available data. Further, this comparison data should be reviewed, ordered, and perfected insofar as possible before the probe experiment.

Viewed in this light, the lunar probe experiment will not be simply a measurement of the composition of one lunar rock sample as a tour-de-force, but instead its characterization for comparison with a host of rocks; such comparison injects into the lunar analytical probe experiment all the accumulated results of the work of the hundreds of analysts who have studied rocks and meteorites throughout the past century, as a means of gaining maximum knowledge about the Moon's surface from one or a few samples perhaps selected by chance before Man can land there and select, inspect and bring back samples.

THE SURFACE OF THE MOON

Physical Characteristics

Topographic and geological maps have already been prepared from photographs of the surface of the Moon and a vigorous photographic mapping program is in progress. The application of standard geological principles permits the recognition of three main divisions of the surface, probably having different ages. The "continental" or highland areas of the Moon are light in color, and studded with mountains, craters, and linear features. More recent than the light-colored highlands are the large dark-colored areas of lower elevation, the maria, which are, for the most part, almost flat. Locally, there are low domes and anticlines, with very gentle slopes. Occasional craters, rare small crater chains, and some linear features occur in parts of the maria. Superimposed on both the highland areas and the maria is a family of craters of apparently younger age than the others in the highland areas, and younger than those which are covered or partly covered by the maria.

Origin of the Lunar Features

The two major hypotheses of the origin of the lunar surface are concerned with (1) meteoritic impact, and (2) volcanic activity. Most experts are prepared to adopt a compromise hypothesis, but opinions about the relative importance of meteoritic impact and of volcanic activity are greatly divergent.

According to the first hypothesis, the lunar surface was shaped by meteoritic impact, and is therefore composed of an unsorted rubble of meteoritic material and impactite resulting from fusion of surface rocks during impact. Most proponents of this hypothesis feel that the maria are composed of extrusive igneous rocks, but an alternative view is that the maria are covered by very fine material which settled from enormous dust clouds raised by the impact of meteorites.

According to the second hypothesis, the flatter parts of the highland areas may represent the original lunar surface, now partly covered by volcanic extrusives,

and the maria are vast areas of extrusive igneous rocks. Although a volcanic origin is ascribed to some of the craters, proponents of this hypothesis agree that many of the craters were caused by the impact of meteorites, and some meteoritic debris may be expected.

Composition of the Lunar Surface

There is as yet no definitive evidence of the composition of the lunar surface, and inferences based on terrestrial rocks and meteorites range from chondritic to granitic compositions. According to both major hypotheses for the origin of the lunar surface features, material of both meteoritic and igneous origin may be expected. According to the meteorite impact hypothesis the surface would be largely covered by material corresponding in composition to a mixture of chondrites, mingled with fragments of carbonaceous chondrites (rare), achondrites, iron meteorites (iron-nickel alloy), and rock dust and glassy impactite resulting from fusion during impact. According to the volcanic hypothesis the light-colored highland areas may be composed of acidic volcanic extrusives such as pumice, rhyolite, or silicic welded tufts, and the dark-colored maria may be covered by dark basaltic lava flows. However, it has been pointed out that radiation damage may cause light-colored rocks to become dark; this and other major differences between the terrestrial and lunar environments makes interpretation of lunar colors in terms of terrestrial rocks rather uncertain. Despite the dark color of the maria, therefore, the proposal that the maria are covered by silicic ash falls or flows merits consideration. Some of the low domes on the maria have been interpreted as serpentinite domes, or alternatively as laccoliths composed of granitic igneous rocks.

Sedimentary rocks and metamorphic rocks comparable to terrestrial types are not expected because of the absence of water and air (serpentinite is here treated as an igneous rock), and this greatly simplifies the business of identifying

lunar rocks as to type by means of a chemical analysis. Still, "sedimentary" rocks of two types may be encountered. The first type would consist of accumulated particles deposited from the enormous dust clouds expected by some proponents of the meteoritic impact hypothesis. The rock so formed would represent a homogenized sample of the lunar surface rock and the meteorite(s) involved in an explosive impact. The second type of sedimentary rock which might be encountered is a lunar weathering product produced in situ from pre-existing igneous or meteoritic material, as a result of radiation damage and spallation caused by the extreme temperature fluctuations. The changes induced by such processes would be dominantly physical rather than chemical.

According to another suggestion, tektites may be debris from meteoritic impacts on the Moon. If this is so, then the tektites have already provided us with a sample of the lunar crust, albeit one somewhat modified by the origin process and passage through the earth's atmosphere. The compositions of tektites are therefore included in this review.

The Sampling Problem

Clearly, interpretation of the significance of the chemical analysis of a single rock sample at the surface of the Moon must be made with caution. Identification of the first rock sampled as a chondrite, for instance, would not prove that igneous rocks are absent on the lunar surface, and identification of the sample as a basalt would not mean that there is little meteoritic material on the lunar surface. This is almost too obvious to be stated, but in view of the heated debates which have developed even when there was no direct evidence available, it is not unlikely that the availability of a chemical analysis of a single sample would engender even more heat, with some persons claiming verification of their hypothesis, and others suddenly discounting the significance of a single sample. One does well therefore to take thought in advance to the question of significance of a single small sample

taken from a large, probably heterogeneous object and consider very carefully what measurements would yield the most significant information.

Ideally the location of the site of the measurement on the Moon should be selected as closely as possible in advance with sample significance in mind, and then the position at which the actual measurement is made should be fixed as precisely as possible. The chemical measurement can then be related not just to the single sample, but by geological inference techniques first to the particular formation on which the probe landed and then more generally.

The highland areas of the Moon are structurally complex. Interpretation of the areal significance of a single measurement of a highland sample would therefore be more difficult than that of a single sample from a mare. In fact, in view of the uniform appearance of the maria, it would seem permissible to take even a single sample, provisionally, to be representative of the whole mare and probably all maria – of course subject to later confirmation. But at present it would appear, for this reason, a sampling point on a mare would give information having a much wider "area of inference" on the Moon's surface than a single sampling point on the highlands. (The situation is entirely different in the case of a manned landing – but this is not our concern here.)

The size of the individual sample analyzed is also important. The volume and shape of the whole-rock sample that must be taken depends on the mineral grain size distribution and texture of the rock. For example, to determine the composition of a medium grained terrestrial rock, one ordinarily takes a fist-sized sample. He need thereafter analyze only a small fraction of this, if he powders the sample and mixes it thoroughly. Alternatively, here on Earth he can prepare two thin-sections, taken at right angles, and determine composition and structure by making mineral grain counts or point-to-point compositional analyses. The first technique (crushing, homogenizing and subsample preparation) is appropriate when

grain size and texture are known, but the second is preferable when, as on the Moon, grain size, texture, etc., are not known in advance; a "traverse" sampling technique can yield valuable information on the rock's texture and grain size as well as on its total composition.

CHEMICAL COMPOSITION OF TERRESTRIAL IGNEOUS ROCKS

While the chemical compositions of terrestrial igneous rocks have a fairly wide range, these compositions are nevertheless constrained within certain well-defined limits because of the chemical combining properties of the elements involved. But within these limits, there is continuous chemical variation among the different rock types. Only eight elements make up nearly 99 weight per cent of most terrestrial igneous rocks. These are: O, Si, Al, Fe, Ca, Na, K, and Mg, and of these oxygen is absolutely predominant. Other elements, termed "minor" elements (up to percent level) or "trace" elements are present only in relatively very small concentrations and therefore cannot control rock structure or mineralogy. Nevertheless, some minor elements vary among the different igneous rocks in such a way that their concentrations are of great diagnostic value. Furthermore, measurements of the isotope concentrations of certain minor elements can provide much additional useful information on rock age, origin, and history.

An average chemical composition for the igneous rocks composing the crust of the earth has been computed by several workers. Results vary depending on how "crust" is defined as well as due to differences in data selected. One result is shown in Table 1. The rock composition is expressed in terms of oxides (as is customary in petrology) but the major element concentrations are also shown. This gives at least a good indication of the levels of concentration of the various elements which must be detected.

Table 1

Average Chemical Composition of All Igneous Rocks

	Weight Per Cent			Element	Percent	
					Weight	Atomic
SiO_2	59.12	F	0.030	O	46.7	59.6
Al_2O_3	15.34	S	0.052	Si	27.7	20.1
Fe_2O_3	3.08	$(Ce, Y)_2O_3$	0.020	Ti	0.6	2.0
FeO	3.80	Cr_2O_3	0.055	Al	8.1	6.1
MgO	3.49	V_2O_3	0.026	Fe	5.1	1.9
CaO	5.08	MnO	0.124	Mg	2.1	1.8
Na_2O	3.84	NiO	0.025	Ca	3.7	1.9
K_2O	3.13	BaO	0.055	Na	2.8	2.4
H_2O	1.15	SrO	0.022	K	2.6	1.4
CO_2	0.10	Li_2O	0.007	H	0.14	2.8
TiO_2	1.05	Cu	0.010			
ZrO_2	0.04	Zr	0.004			
P_2O_5	0.30	Pb	0.002			
Cl	0.048					

The specific igneous rocks which have been most frequently suggested as common lunar surface materials are serpentinite, basalt, silicic welded tuff (including rhyolite, pumice, etc.), and granitic rocks (belonging to the same chemical family as the tuff). Rocks which legitimately carry each of these names may, unfortunately, have a range of chemical compositions. There are available many collations of the compositions of these rock types, and at least as many "average" values for each have been calculated. Some compositions for these igneous rocks believed to be rather representative are tabulated in Table 2 in terms of their oxides. Their compositions recalculated in terms of element concentration are illustrated in Figures 1 and 2. In addition to the rock types listed above, the average value of peridotite is included in the table, because serpentinite is usually developed from peridotite.

The table illustrates that distinct chemical differences do exist among the different rock types, but the significant chemical differences can perhaps be seen more clearly in chemical variation diagrams. Some of these have therefore been prepared and are discussed below. Differences in the chemical compositions of meteorites, and differences between rocks and meteorites will also be indicated, after a discussion of meteorite composition.

CHEMICAL COMPOSITIONS OF METEORITES

There are fewer types of meteorites than there are types of igneous rocks, and of these consideration of the chondrites is probably the most important for the present problem. The chondrites are the commonest of all meteorites and, according to one authority, "outer space is evidently populated by chondritic meteorites almost to the exclusion of other types." The carbonaceous chondrites, a rare variety of the family, differ chemically in having high water and carbon content. Other meteorites which should be considered are the achondrites, and the iron meteorites. The stony-iron meteorites and the irons can readily be distinguished chemically by

Table 2

Average Chemical Compositions of Selected Igneous Rocks

	S	P	B	G	WT
SiO_2	35.8	43.95	48.80	70.18	73.15
TiO_2	0.004	0.10	2.19	0.39	0.14
Al_2O_3	0.148	4.82	13.98	14.47	12.13
Fe_2O_3	–	2.20	3.59	1.57	1.12
FeO	5.61	6.34	9.78	1.78	0.66
MnO	0.095	0.19	0.17	0.12	0.04
MgO	39.4	36.81	6.70	0.88	0.13
CaO	0.074	3.57	9.38	1.99	0.71
Na_2O	–	0.63	2.59	3.48	4.01
K_2O	Tr	0.21	0.69	4.11	5.27
H_2O	12.30	1.08	1.80	0.84	1.91
P_2O_5	–	0.10	0.33	0.19	0.00
	99.44	100.00	100.00	100.00	99.27

S. An average serpentinite

P. Average peridotite

B. Average plateau basalt

G. Average granite

WT. A sample of glassy welded tuff from Yellowstone National Park

the nickel-iron alloy which they contain, and so these will not be considered further here. However, tektites are included here among the meteorites, despite the uncertainty about their true origin. Table 3 lists the chemical compositions of some meteorites in terms of oxides. Their compositions in terms of elements are illustrated graphically in Figures 1 and 2.

MAJOR ELEMENT VARIATIONS IN IGNEOUS ROCKS AND METEORITES

The continuous chemical composition variation among terrestrial igneous rocks has already been mentioned. This variation in composition is conventionally illustrated in chemical variation diagrams, in which various oxides or elements are plotted against a selected parameter. The SiO_2 content of igneous rocks varies appreciably from one rock type to another, as shown in Table 2, and the SiO_2 percentage of a rock has been widely used as the parameter representing "basicity" or "acidity" in chemical variation diagrams.

In Figure 1, the average weight percentages of the elements contained in the rocks and meteorites tabulated in Tables 2 and 3 are plotted against the weight percentage of Si in the rocks. The averages for igneous rocks are plotted as circles, and for meteorites are plotted as squares. The compositions of the igneous rocks are connected by a line, which represents the chemical variation of an average igneous rock series ranging in composition from serpentinite, through peridotite and basalt, to the granitic rock family which includes granites and welded tuff. Each of these rock types may occupy an appreciable range of composition around the plotted average value, and the shaded areas I, II, III and IV illustrate the known ranges of composition for families of rocks which are called serpentinite, basalt (or gabbro), granite (or rhyolite, or silicic welded tuff, or pumice, etc.) and achondrite. Figure 1 shows that the three igneous rock families are readily distinguished from each other on the basis of major element contents. The diagrams

Figure 1A - 1G: Chemical variation diagrams showing the average compositions of igneous rocks (circles) and of meteorites (squares). S - serpentinite, P - peridotite, B - basalt, G - granite, WT - welded tuff, CC- carbonaceous chondrite, C - chondrite, A - achondrite, T - tektite. The lines connecting the circles represent the average chemical variation of the igneous rock series. The shaded areas indicate the composition ranges of the igneous rock families: I - serpentinites, II - basalts, and III - granites and rhyolites; Area IV shows the range for pyroxene-plagioclase achondritic meteorites.

Figure 2A, 2B: Chemical variation diagrams showing critical chemical differences among igneous rocks (circles) and meteorites (squares). The shaded areas indicate the composition ranges of the igneous rock families: I - serpentinites, II - basalts, III - granites. Once again Area IV represents the pyroxene-plagioclase achondrites. A key for the rocks and meteorites plotted is given in the legend of Figure 1.
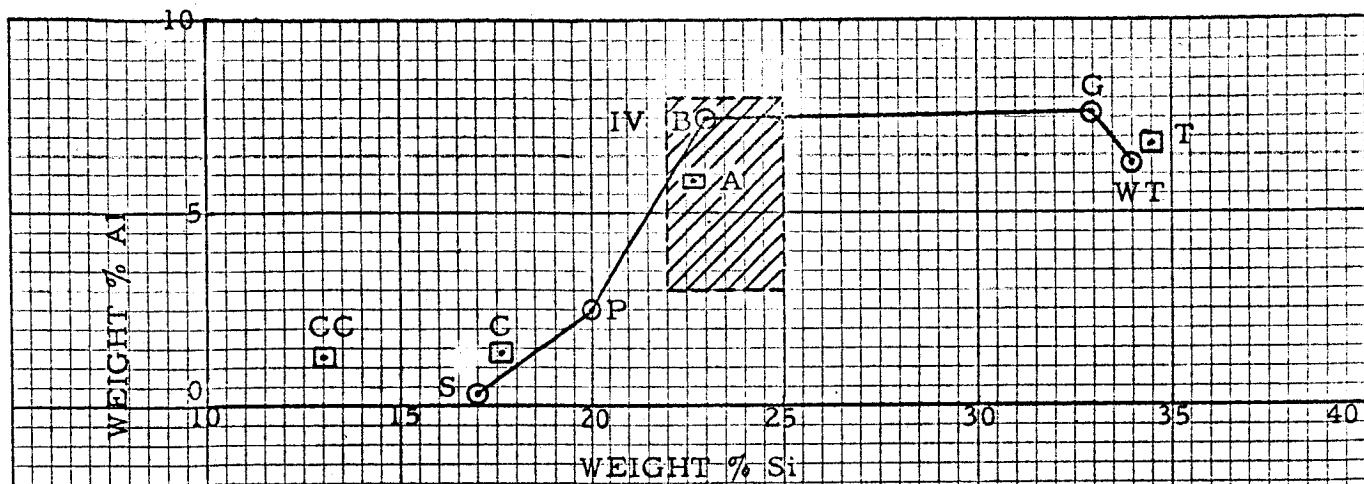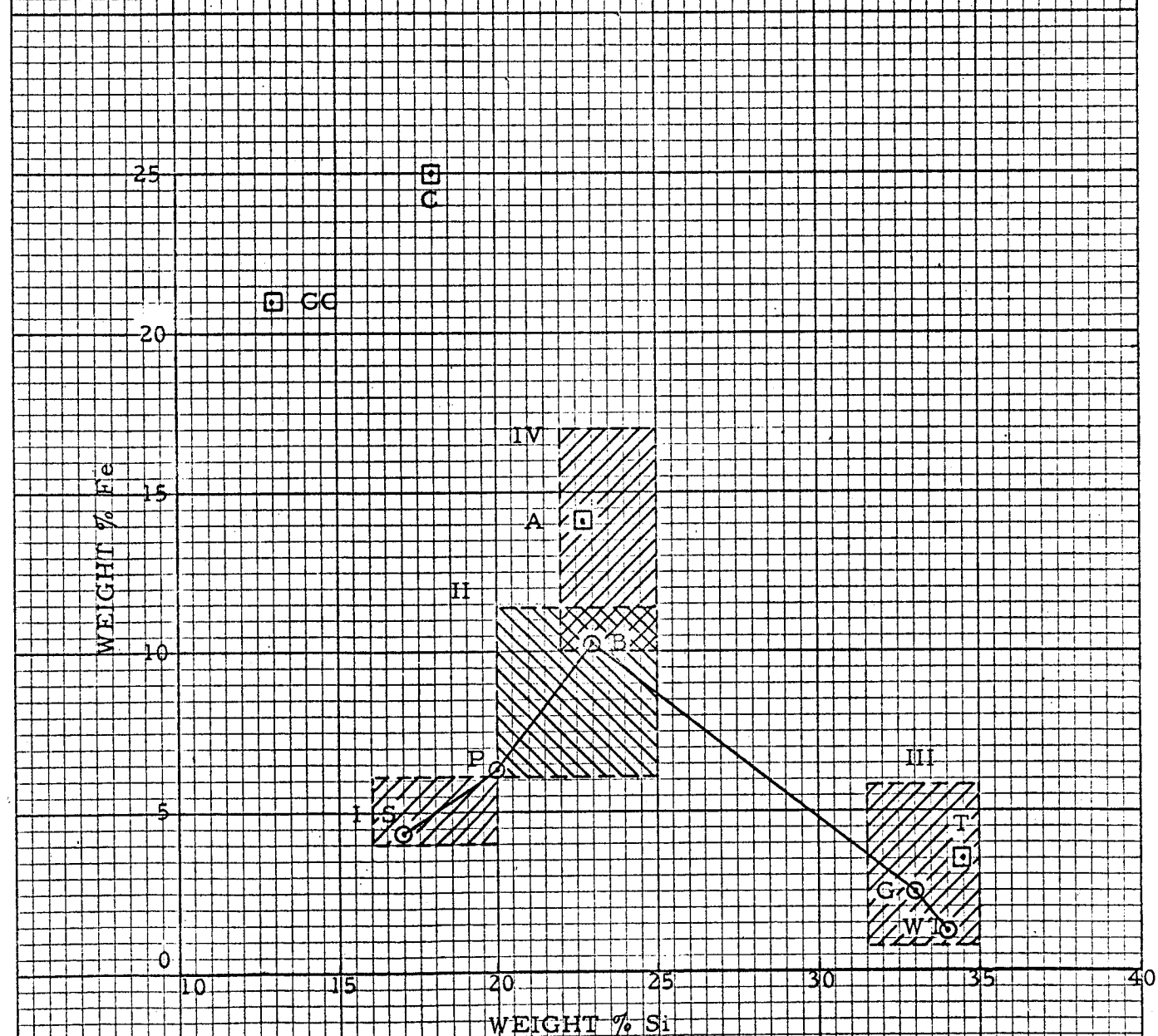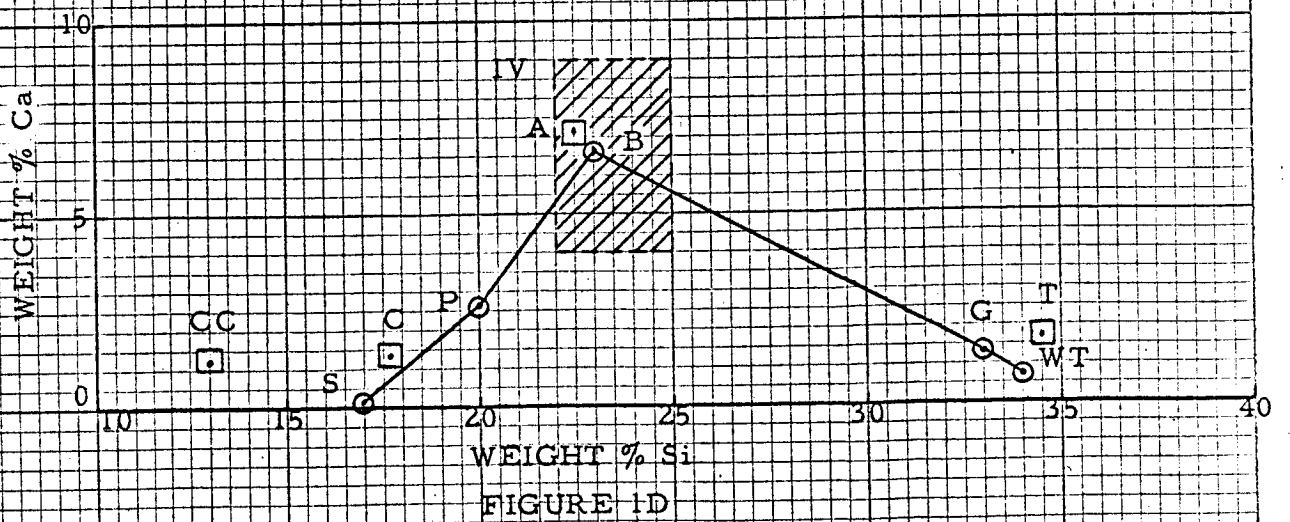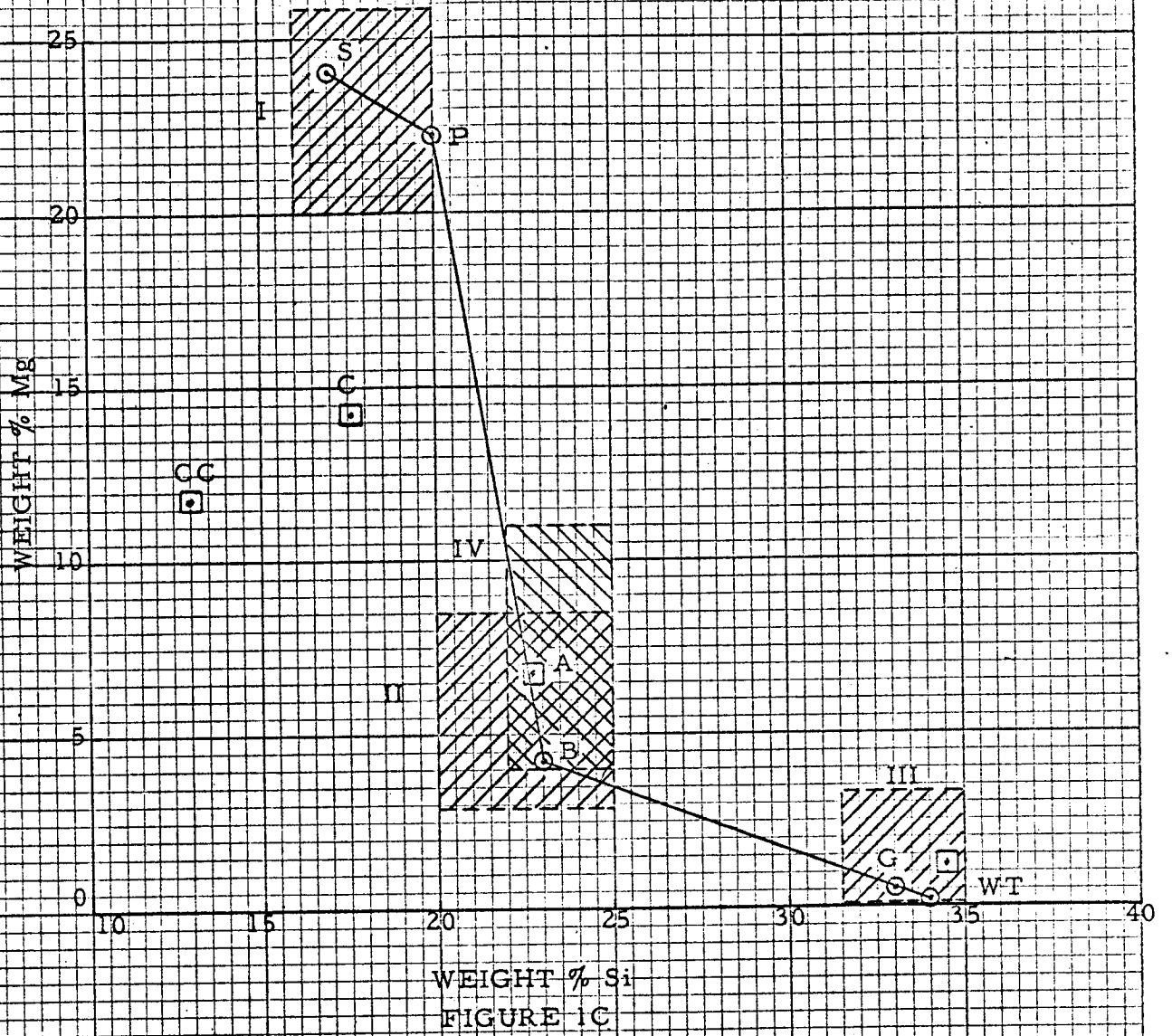
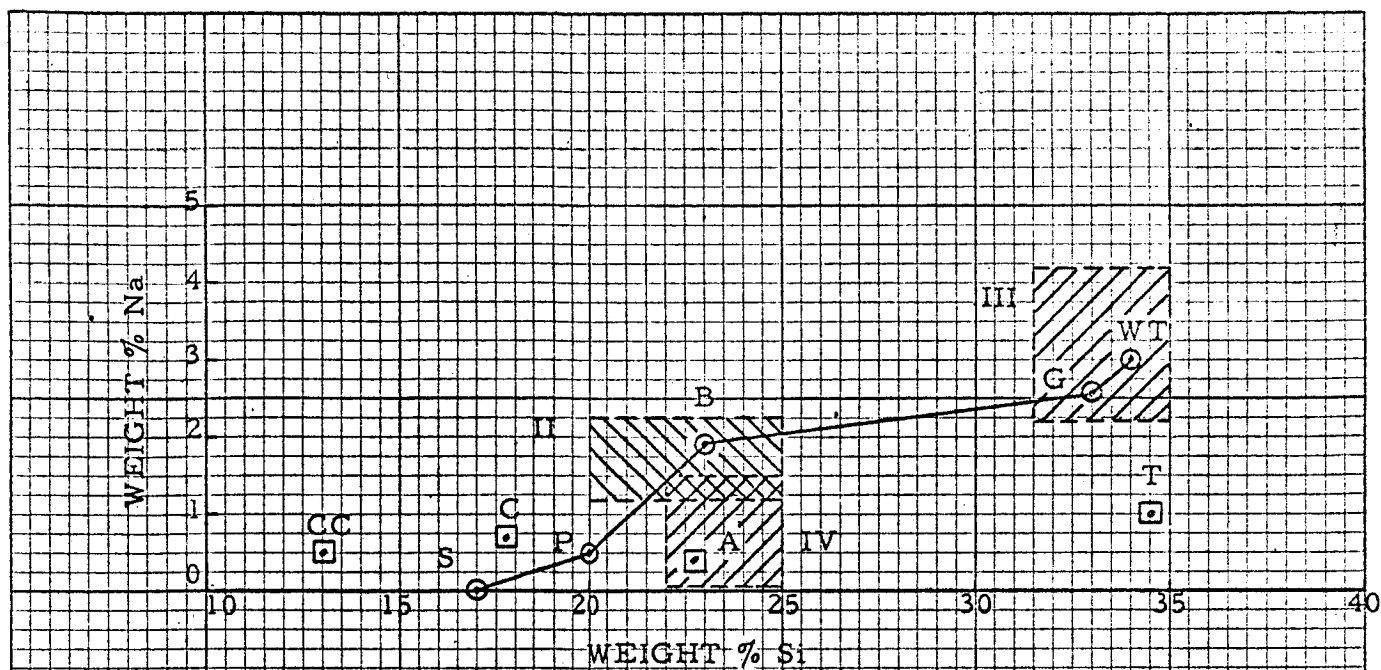FIGURE 1A

WEIGHT % Si

FIGURE 1B

WEIGHT % Si

FIGURE 1C

WEIGHT % Si

FIGURE 1D

FIGURE 1E

FIGURE 1F

FIGURE 1G

WEIGHT % Na

WEIGHT % K
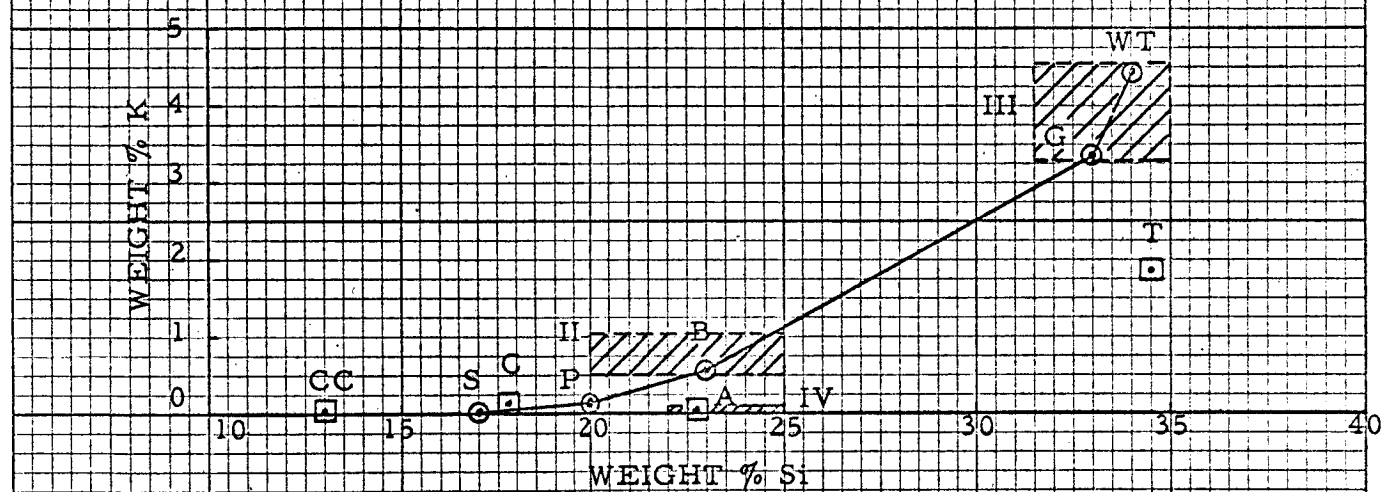
FIGURE 2A
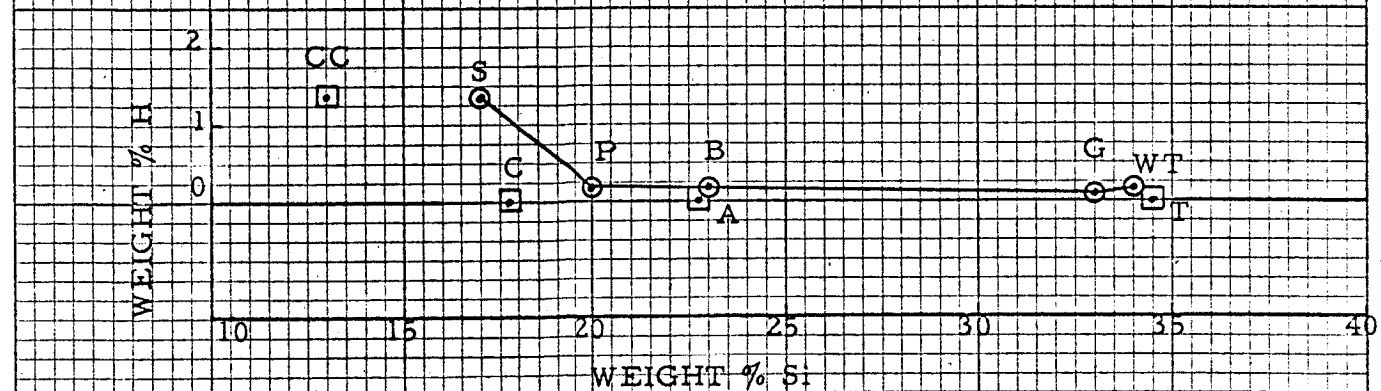
WEIGHT % Fe

WEIGHT % Mg

FIGURE 2B
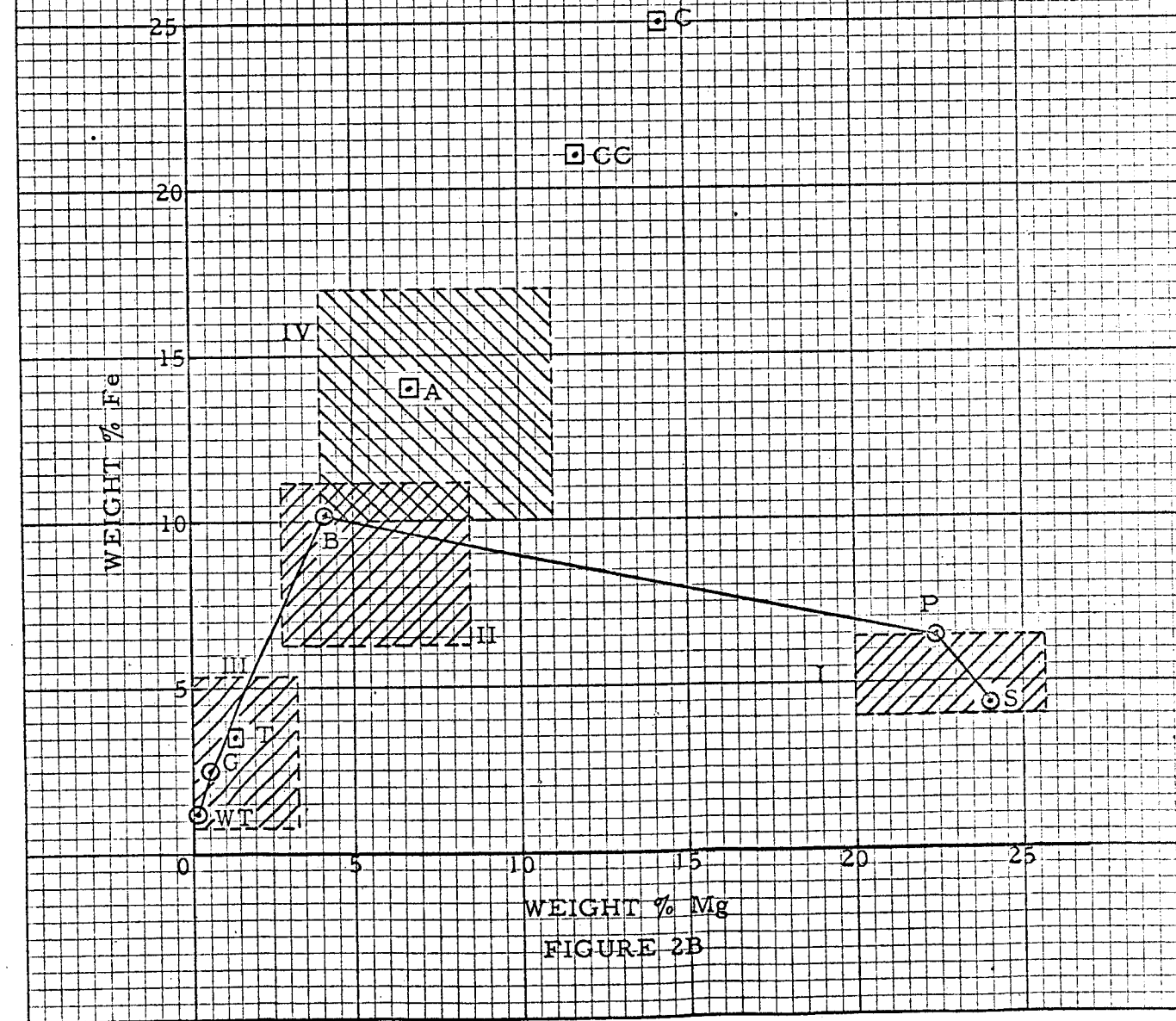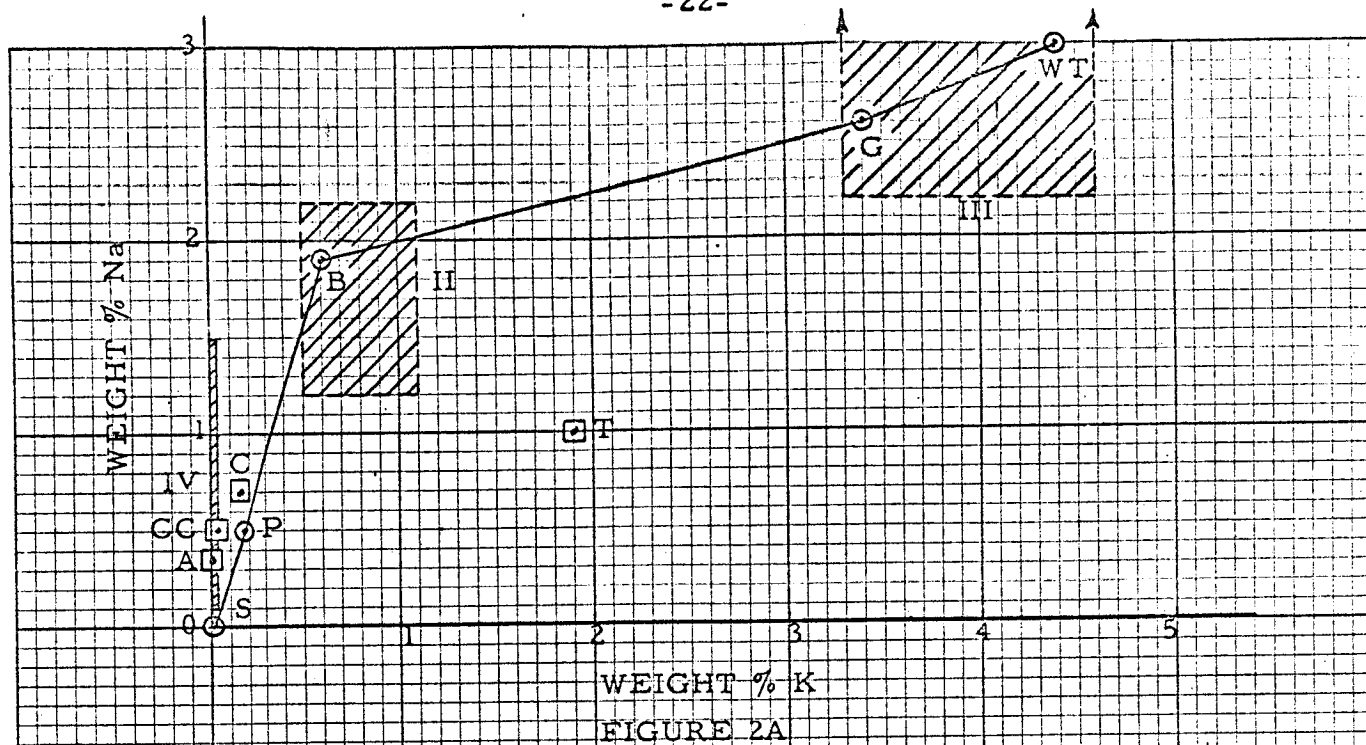
Table 3

Average Chemical Compositions of Meteorites (weight per cent)

	CC	C	A	T	I
Fe	0	11.76	0.9	-	90.23
Ni	0	1.34	0	-	8.54
Co	0	0.08	0	-	0.49
FeS	3.66	5.73	0	-	0.33
SiO_2	27.81	38.04	49	73.87	0.08
TiO_2	0.08	0.11	-	0.75	--
Al_2O_3	2.15	2.50	11	12.69	--
MnO	0.21	0.25	-	0.10	0
FeO	27.34	12.45	17	4.16	0
Fe_2O_3	---	-----	-	0.47	0
MgO	19.46	23.84	11	2.18	--
CaO	1.66	1.95	10	2.23	--
Na_2O	0.63	0.98	0.5	1.38	--
K_2O	0.05	0.17	-	2.28	--
P_2O_5	0.30	0.21	-	-----	P=0.34
H_2O	12.86	----	-	-----	--
Cr_2O_3	0.36	0.36	-	-----	Cr=0.02
NiO	1.53	----	-	-----	0
CoO	0.07	----	-	-----	0
C	2.48	----	-	-----	Low
	101.01	99.77	99.4	100.11	100.07

CC. A carbonaceous chondrite
 C. Average of superior analyses of chondrites
 A. Average pyroxene-plagioclase achondrite
 T. Average tektite
 I. Canyon Diablo iron meteorite. Also contains 0.04 % Cu. (Buddhue, J.D.,
    Pop. Astron. 58, 190 (1950)

show that the meteorites do not conform to the same orderly sequence of chemical variation and distinction must be made on the basis of specific element concentrations.

It is believed to be very unlikely that the achondrites form a significant part of the lunar surface; still, it is entirely possible that the sample measured might turn out to be an achondrite. This could present real difficulties because the range of compositions occupied by the achondrites overlaps considerably with that of the basaltic rocks, which it is thought may be one of the major lunar surface constituents.

The achondrites occupy a rather wide range of chemical composition, and they include several different mineralogical types. They may be characterized chemically by their CaO content and by their ratios FeO/MgO. The most common achondrites are the pyroxene-plagioclase achondrites (see Table 3 for an average value), and so it is their range of chemical composition that is indicated by the area IV in Figures 1 and 2.

Most meteorites can easily be distinguished from the igneous rocks on the basis of the concentrations of the elements Fe, Mg, Na and K. In Figure 2, the compositions of the igneous rocks and of the meteorites are compared in two diagrams, Na vs. K. and Fe vs. Mg. The key for the circles, squares and shaded areas is the same as for Figure 1.

It is not possible in this report to examine in detail the ranges of composition of every conceivable rock type which might be encountered on the surface of the Moon - although certainly this should be done at some stage before the lunar probe work begins. The diagrams illustrating the manner in which the concentrations of certain elements vary in certain rocks which it is thought might be expected on the Moon (Figures 1 and 2) give only average values. But the ranges of composition are given for rocks classified in the families called serpentinite, basalt, granite and achondrite, and these demonstrate that the measurement of only a few elements would suffice to distinguish between them. But because it is impossible to rely upon the proposition

that these are the only likely rocks upon the Moon, attention must be given to the extent of overlap in composition which other types of rock have with these, which have been considered until now in most detail. This emphasizes once again the need to characterize the lunar sample in as much detail, chemically, as is possible. The probe analysis will be made on unknown material, and although there have been many intelligent guesses as to what this material might be, we must not lose sight of the fact that its actual composition is unknown, and must be treated accordingly. The intelligent guesses as to what will be found can be used only as a guide – albeit a very useful one.

Chemical differences among igneous rocks and meteorites

The positions of the shaded areas in Figure 1 indicate that the three families of igneous rocks which have been proposed as representatives of lunar rocks can be distinguished from each other readily by their Si content alone: indeed, one basis for the classification of igneous rocks is the amount of silica they contain.

Serpentinite (Area I) can be distinguished from the other igneous rocks by its low Al (Figure 1A), high Mg (Figure 1C), low Na and K (Figures 1E and F), and high H (Figure 1G).

Basalt (Area II) can be distinguished from the other igneous rocks by its high Fe (Figure 1B), intermediate Mg (Figure 1C; note small overlap with some granitic rocks), high Ca, and intermediate Na and K (Figures 1E and 1F).

The granitic rocks (Area III) can be distinguished from the other igneous rocks by their low Mg (Figure 1C; note small overlap of some granitic rocks with some basaltic rocks), and high Na and K (Figures 1E and F).

The achondrites (Area IV) overlap basalts in composition but might be distinguished by FeNi content.

The iron meteorites are readily distinguished from other meteorites and the igneous rocks (Table 3). Iron containing stones might also be determined by Fe Ni

content and also by sulfur.

Figure 1 confirms that the stony meteorites can ordinarily be distinguished from each other on the basis of their silica content, but only the carbonaceous chondrites can be distinguished from the igneous rocks in this way. The specific chemical differences between the meteorites and the igneous rocks are shown in Figure 1, but the distinctions are perhaps more clearly visible in Figure 2, in which is plotted the average values of the ratios Na/K and Fe/Mg for the various rocks, as well as the absolute values of Na, K, Fe, and Mg.

Figure 2A confirms that the meteorites (except some achondrites) can be distinguished from basaltic and granitic rocks by their low alkali content, and that tektites can be distinguished from granitic rocks (the only igneous rocks they are likely to be confused with, see Figure 1 for Si content) by their relatively low alkali content. Serpentinite contains virtually no alkalis (Table 2), and is therefore distinguishable from the meteorites on this basis as well. However, a distinction among the meteorites themselves cannot be based on alkali content.

Figure 2B confirms that the meteorites (except some achondrites) can be clearly distinguished from serpentinite, as well as from the basaltic and granitic rocks, on the basis of their Fe content. The meteorites have a much higher Fe/Mg ratio than does serpentinite. On the basis of Fe and Mg contents, Figure 2B confirms that chondrites are readily distinguishable from achondrites, and probably distinguishable from carbonaceous chondrites. Only the carbonaceous chondrites and serpentinites contain more than a very small amount of water (Figure 1G), so distinction between the carbonaceous chondrites and the others should be made readily.

In summary, it may be concluded that it may be possible to distinguish among the few igneous rocks and meteorites which have been most often proposed as major lunar surface materials by measuring the concentrations of just three elements:

Si, Fe, and Na (or K). The additional measurement of water, or of H, would immediately indicate the presence or absence of the only likely hydrated materials, serpentinite or carbonaceous chondrite. Determination of additional elements would serve to confirm the identification made (Figures 1 and 2), and would be necessary to provide enough information about the rock to permit the mineralogical constitution of the rock to be estimated. The more elements which can be measured, the more precise and detailed will be the characterization of the rock concerned. Furthermore, there is still a substantial possibility that the sample analyzed on the surface of the Moon will have no known counterpart among the meteorites or the terrestrial igneous rocks.

TRACE ELEMENT VARIATION IN IGNEOUS ROCKS AND METEORITES

Data on the concentrations of trace elements in igneous rocks and meteorites are not as abundant as the data for major elements, yet they are quite extensive. It would be possible to compile the data for all elements and from it to construct diagrams similar to those given for major elements to illustrate the differences between trace element concentrations in igneous rocks and meteorites, but this would be a major undertaking because analyses for the trace and microtrace elements are very spotty in quality so that such a compilation is of little value unless at the same time an investigation of each measurement is made to evaluate it as to quality.

Table 1 gives data on some of the trace elements of possible interest, but this list is illustrative only, not complete. Certain trace elements can be of direct value in distinguishing between igneous rocks and meteorites, while others can yield information about the rate of generation of heat by radioactive decay in lunar materials, or about the age of the sample, or its origin or thermal history.

The chondrites are readily distinguished from most igneous rocks by their

higher content of Ni and Cr. Table 1 shows that the concentrations of NiO and Cr_2O_3 in the average igneous rock are 0.025 and 0.055 weight per cent respectively, whereas the average chondrite (Table 3) contains 1.3 weight per cent or NiO and 0.36 weight per cent of Cr_2O_3. Other trace elements which may help to distinguish between chondrites and igneous rocks expected on the Moon are C, which occurs in more than trace amounts only in carbonaceous chondrites (Table 3), and S, which is present in appreciable quantities in chondrites (Table 3) whereas in basalts and granites it occurs only in trace amounts.

If the concentration of any one of the radioactive elements U, Th, K, Rb and Sm could be measured with sufficient sensitivity, this measurement by itself would permit a first classification of the rock as chondritic, basaltic or granitic — as is shown by the data listed in Table 4.

Measurement of the concentrations of radioactive isotopes and their daughter nuclides could provide "apparent ages" for the sample. If it is only possible to attempt to obtain an age by one technique, the K-Ar decay should probably be used, because if any of the "most plausible" rocks is actually encountered, K will very certainly be much more abundant in it than the other radioactive elements, and its daughter isotope the noble gas ^{40}Ar will be most easy to liberate from the rock and least contaminated with "original" ^{40}Ar. Rb/Sr and/or U/Pb "ages" would be necessary to confirm the K/Ar apparent age. In a more thorough study, one would also attempt to determine "cosmic ray exposure ages" using ^{10}Be, ^{26}Al and other isotopes of very small abundance.

The existence of "isotope effects" in chemical processes operating on Earth has led to the development of techniques for the measurement of temperature of rock genesis, etc., involving the determination of isotope ratios in the elements C, O, S, and H. The isotope effects are however quite small and their measurement requires extremely precise measurements of isotope ratios. It would therefore appear at

Table 4

Radioactive Element Concentrations in Weight Per Cent

Element	Chondrites	Basalts	Granites
U	1×10^{-6}	5×10^{-5}	4×10^{-4}
Th	2×10^{-6}	3×10^{-4}	2×10^{-3}
K	0.085	0.5	4.0
Rb	5×10^{-4}	2×10^{-3}	2×10^{-2}
Sm	1×10^{-4}	2×10^{-4}	6×10^{-4}

K^{40} = 0.0119 % of K

Rb^{87} = 28% of Rb

Sm^{147} = 15% of Sm

first inspection that the performance of such studies on lunar samples should await the time when samples can be collected there and returned to terrestrial laboratories.

There is, however, the fundamental question of the degree of similarity between "moon stuff" and terrestrial materials, meteorites, and solar material in its nuclidic abundances, which in many ways provide better information on origin and history than do elemental abundances. Since isotopes are only very slightly fractionated by natural processes (as mentioned in the preceding paragraph), isotope ratios can give reliable information on nuclidic abundances in the original material from which the Moon (or Earth or meteorite) was formed. Measurements of isotope ratio of moderate precision would suffice to determine whether the isotope ratios of H, Li, C, O, N, Ne, Si, Fe, etc., were (as we anticipate) in the terrestrial-meteoritic range or not; therefore such measurements should be attempted on one or more of the above elements.

INTERPRETATION OF A SINGLE CHEMICAL ANALYSIS

The object of analyzing the rocks on the surface of the Moon is to identify them, in order to provide information on rock properties useful in planning manned landings and expeditions, and also on the origin of the Moon and the processes which have shaped its surface. Given a complete chemical analysis of a lunar sample, the next step would be to compare it with all available analyses of rocks and meteorites. A procedure for comparison and identification has been outlined in the preceding pages; it has been shown that a chemical analysis can provide a means of distinguishing among the various types of igneous or meteoritic material which may be expected on the lunar surface. But as was also mentioned, the chemical analysis does not tell us at once what the mineralogical constitution of the material is. The chemistry of a rock does not provide a unique solution for its mineralogy.

Several rocks composed of different mineral assemblages may have almost identical chemical compositions. A rock may be composed almost entirely of glass, or of glass containing some crystalline material, or of large grains of minerals, or of one mineral. A chemical analysis tells us little about this. On the other hand, if the mineralogy of a rock is known completely, then the chemical composition is uniquely determined — within certain compositional ranges. The mineralogy and texture of a rock are controlled by the chemical composition, and by the physical conditions of formation of the rock. Information on the mineralogy and texture of a rock thus can provide information about its manner of formation. Such information is, of course, most important also from the engineering standpoint.

As Tables 2 and 3 illustrate, it is not easy to recognize the significant chemical differences among rocks by comparing the chemical analyses of rocks listed as oxides. Too many variables are involved. But there is in general use a method for converting rock chemical analyses into rock mineral "norms" which permits the analyses to be compared with other rock analyses in a meaningful fashion. The analyses expressed in terms of oxides are recalculated into a set of standard mineral molecules, which have been chosen in such a way that the calculations are simple, and that the "normative" minerals and mineral assemblages correspond insofar as possible to those actually occurring in real rocks having the same chemical composition. The actual mineral composition of the rock is called the "mode"; the standard mineral molecule composition calculated from the chemical abundances is called the "norm". For many igneous rocks, the norm is remarkably similar to the mode.

Complete details for the calculation of the norm of a rock are given in an appendix. In making the calculation, the compositions of the "standard" mineral molecules are taken to be invariant (while in nature substitution occurs) - as for

example, albite, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$; acmite, $Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$; ilmenite, $FeO \cdot TiO_2$.
The complete list is given in the Appendix. The general procedure is as follows:

1. The oxides present in small quantities are used to form certain standard accessory minerals.

2. All K_2O and all Na_2O are allocated to standard orthoclase and albite feldspar molecules respectively, and all or part of the CaO to anorthite (depending on the relative amounts of CaO and Al_2O_3 remaining).

3. Any CaO remaining, and FeO and MgO are used to form standard pyroxene molecules.

4. If any SiO_2 is left over at this stage, it becomes quartz. But if there was insufficient SiO_2 to convert all of the FeO and MgO to pyroxenes, some of the pyroxene is changed to olivine. Further, for some rocks, it may be necessary to convert albite and ortho-clase to feldspathoids in order to balance the available SiO_2.

5. There are several paths in the calculation alternative to the above sequence set up to deal with the rarer rocks containing, for example, an excess of Na_2O; but the steps outlined above are the ones most commonly used.

The result of a calculation of the above type is the "norm", a list of standard minerals of fixed composition and including quartz, albite, orthoclase, anorthite, pyroxene, olivine (if there is no quartz in the norm), feldspathoids (if there is no quartz in the norm), and various accessory minerals. Quartz, the feldspars, the pyroxenes and olivines together, of course, make up a high proportion of all igneous rocks; in fact, igneous rocks are classified on the basis of their modal quartz and feldspar content and composition, and for many igneous rocks the quan-tities of these minerals in the norm approximate very closely to the quantities in

the mode. <u>Normative quartz and feldspar, therefore, may be used to classify igneous rocks</u>. Note that the amounts of albite and orthoclase feldspars which appear in the calculated norm depend upon the amounts of Na_2O and K_2O in the analysis, and the amount of normative anorthite depends upon the amount of CaO and Al_2O_3 in the analysis. Calculation of the accessory minerals in the norm uses up some of the CaO and FeO before calculation of the major normative minerals, and the amount of quartz in the norm, or the degree of undersaturation if there is insufficient SiO_2, depends upon the amounts and relative proportions of the other major elements after adjustment for the accessory minerals. The accuracy of the calculated norm for a lunar rock sample will thus depend in particular upon the accuracy of measurement that can be achieved for Na and K, which are not likely to be present in very high concentrations (Figure 2).

The procedure for the calculation of the norm of a lunar sample will, furthermore, probably have to be modified compared to the usual procedure given in the Appendix, because the lunar analysis will not be as complete in some details as the usual analyses of rocks. Chemical analyses of terrestrial rocks usually include determinations of the concentrations of 13 elements, and this provides an adequate basis for calculation of the norm. If additional trace elements have been measured, such as BaO, SrO, ZrO_2, etc., these can be incorporated into the normative calculation, but the result is not greatly affected. Computer programs are available for the calculation of norms from a list of only 10 oxides, and the results so obtained are adequate for routine work. However, the ratio of FeO/Fe_2O_3 (ferrous/ferric iron) in an igneous rock has a significant effect on the calculated norm. This ratio will not be available from the <u>in situ</u> analysis of a lunar sample, and the procedure for the normative calculation will have to be modified accordingly.

The norm calculation can also provide a valuable indication of the mineralogical composition of the silicate fraction of meteorites (except for the carbonaceous

chondrites), but here again problems arise in the interpretation of an in situ lunar
analysis. The iron in meteorites is distributed between a metallic nickel-iron
alloy, ferrous iron combined in silicate minerals (FeO), and sulphide minerals
(commonly troilite, FeS). Only the iron combining with oxygen, hence, only the
FeO, combined in the silicate fraction is of significance in the calculation of the
norm. It will also be necessary to ignore the Ni detected in the analysis when
computing the norm, assuming that this probably is combined in the metallic frac-
tion of the meteorite rather than in the silicate fraction. Measurement of S would
give an indication of the amount of iron contained in sulphide minerals, but dis-
tinction between metallic iron and that combined in silicates would be difficult.

The lack of knowledge of the oxidation state of the iron in the lunar sample
is the first major problem in calculating a norm from an analysis. A second
problem will arise if the sample analyzed turns out to be either a serpentinite
or a carbonaceous chondrite. The norm could be calculated, but for these rocks
it would have significance only as a basis for comparison of the sample with other
similar rocks. It would not give the true mineralogy of the sample, because the
standard mineral molecules of the norm include no hydrated minerals, whereas
carbonaceous chondrites and serpentinites are composed almost entirely of hydrated
minerals (note the high water contents of these rocks in Tables 2 and 3).
Serpentinites are composed largely of the mineral serpentine, and carbonaceous
chondrites are composed largely of amorphous hydrated silicate or of serpentine,
together with small amounts of organic compounds. It is possible to work out a
modified normative calculation involving the mineral serpentine, so that the
norms of serpentinites and carbonaceous chondrites would approximate the mineral-
ogical composition; modifications of this kind have been adopted for terrestrial
metamorphic rocks which contain hydrated phases not included in the standard
normative minerals. However, there would seem to be little point in doing this for

these two rocks; the chemical analysis would be sufficient for their recognition, and their analyses can be compared straightforwardly with available analyses of similar rocks. The norms of all other rock types which might be encountered should be worked out, however, and some means of coping with the problem of unknown oxidation state of iron must be devised.

The simplest, and probably quite effective method of treating the iron problem would be to select FeO/Fe_2O_3 values on the basis of the available analyses of similar rocks. To do this the first step would be to decide what type of rock was involved, by using the methods already outlined (Figures 1 and 2). The analysis of the unknown could then be compared with all available analyses of similar rocks or meteorites until the closest match was found. Then, for a sample which was interpreted as being an igneous rock the ratio of FeO/Fe_2O_3 in the matching rock would be adopted, after which the norm could be worked out in the usual way. For a meteorite, the iron would have to be divided between metallic iron, sulphide, and ferrous oxide, by comparison with other analyses of knowns until a closely matching analysis was found, and then the norm would be worked out only for the silicate fraction remaining after the iron allocated to metal and sulphide had been subtracted, along with the nickel and other metal phase and sulfide phase elements. The values obtained for nickel and sulphur in the analysis would be of great help in making the comparison between the sample analyzed and other meteorites, and in deciding what fraction of the analyzed sample should be allocated to the silicate part of the meteorite.

As previously noted, the value of the norm is two-fold; it provides an approximation of the mode of a rock, that is its actual mineralogy, and it makes easier the quantitative comparison of the analysis with those of other rocks. In addition, it is useful for the detection of analytical errors gross enough to result in "impossible" rock types. The norm could therefore be a useful guide for the design

of later probes intended to investigate directly the mineralogy of lunar surface materials, in addition to their chemistry. One of the ways in which useful comparisons could be made between the unknown sample analyzed and terrestrial igneous rocks is by calculating from the norm the Differentiation Index. This index is defined as the sum of its normative salic minerals (see Appendix), and it is used as a parameter in chemical variation diagrams for the comparison of igneous rock series (compare the use of Si in Figure 1). A great advantage of the Differentiation Index compared to other parameters used in chemical variation diagrams is that such diagrams are already available in which 5,000 superior chemical analyses of terrestrial igneous rocks have been plotted in terms of their oxide contents versus their Differentiation Indices. Thus, given the chemical analysis and calculated norm of a lunar sample, direct and easy comparison with a large number of terrestrial igneous rocks, covering the whole range of igneous chemistry, will be possible.

REFERENCES

There is a very extensive bibliography on the chemical composition of rocks and meteorites. Hereinbelow, only some representative titles are listed, with emphasis on recent compilations and evaluations. Extensive bibliographies are given in many of these papers.

Barth, T.F.W., 1962. Theoretical petrology, 2nd edition. John Wiley & Sons, Inc., New York.

Boyd, F.R. 1961. Welded Tuffs and flows in the rhyolite plateau of Yellowstone Park, Wyoming., Geol. Soc. Amer. Bull. 72, 387 - 426.

Brown, H., and Patterson, C. 1948. The composition of meteoritic matter. III Phase equilibria, genetic relations, and planet structure. Jour. Geol. 56, 85 - 111.

Clarke, F.W., and Washington, H.S. 1924. The composition of the earth's crust. U.S. Geol. Survey, Profess. Paper 127.

Daly, R.A. 1942, in "Handbook of physical constants", Geol. Soc. Amer. Special Paper 36, 2.

Daly, R.A. 1943. Meteorites and an earth model. Geol. Soc. Amer. Bull. 54, 401 - 456.

Green, J. 1959. Geochemical table of the elements for 1959. Geol. Soc. Amer. Bull. 70, 1127 - 1184.

Johanssen, A. 1939. A descriptive petrology of the igneous rocks, 2nd edition. Chapter 8 in Volume 1. University of Chicago Press.

Mason, B. 1958..Principles of Geochemistry. 2nd edition. John Wiley & Sons, Inc., New York.

Mason, B. 1962. Meteorites. John Wiley and Sons, Inc., New York.

Nockolds, S.R., 1954. Average chemical compositions of some igneous rocks. Geol. Soc. Amer. Bull. 65, 1007 - 1032.

O'Keefe, J.A. (ed.) 1963. Tektites. University of Chicago Press.

Olsen, E.J. 1961. High temperature acid rocks associated with serpentinite in eastern Quebec. Amer. Jour. Sci., 259, 329 - 347.

Palm, Ann, and Strom, R.G. (Jan. 1962) Elemental Abundances of the Lunar Crust. Space Science Lab, University of California (Berkeley) Research Reports, Series 3 Issue 4 (NASANsG - 145 - 61).

Thornton, C.P., and Tuttle, O.F. 1960. Chemistry of igneous rocks. I Different- iation Index. Amer. Jour. Sci., 258, 664 - 684.

Urey, H.C. and Craig, H. 1953. The composition of the stone meteorites and the origin of the meteorites. Geochim. et Cosmochim. Acta, 4, 36 - 82.

Wahl, W. 1951. The statement of chemical analyses of stony meteorites and the interpretation of the analyses in terms of minerals. Miner. Mag., 29, 416 - 426.

APPENDIX I

CALCULATION OF THE NORM

Certain constituents, as calculated, enter only into molecules which are incapable of change, whatever the chemical composition of the rock. Thus ZrO_2 appears only in standard zircon, P_2O_5 in apatite, etc. Other constituents may enter different mineral molecules according to the amounts of other constituents present. Potash may form orthoclase, leucite, or kaliophilite, and soda form albite or nephelite, according to the amount of available silica.

Alumina, unless in excess of combined alkalies and lime, always unites in the ratio of 1:1 with potash, soda, or lime in the salic minerals orthoclase, leucite, kaliophilite, albite, nephelite, and anorthite. In these minerals any mention of potash, soda, or lime, therefore, implies an equal number of molecules of alumina. Only the lime in anorthite is salic; the excess is femic.

Normative Mineral Molecules
(Salic Group)

Mineral	Formula
Quartz (Q)	SiO_2
Corundum (C)	Al_2O_2
Zircon (Z)	$ZrO_2 \cdot SiO_2$
Orthoclase (or)	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$
Albite (ab) F	$Na_2O \cdot Al2O_3 \cdot 6SiO_2$
Anorthite (an)	$CaO \cdot Al_2O_3 \cdot 2SiO_2$
Leucite (lc)	$K_2O \cdot Al_2O_3 \cdot 4SiO_2$
Nephelite (ne) L	$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$
Kaliophilite (kp)	$K_2O \cdot Al_2O_3 \cdot 2SiO_2$
Halite (hl)	$NaCl$
Thenardite (th)	$Na_2O \cdot SO_3$
Sodium carbonate (nc)	$Na_2O \cdot CO_2$

Normative Mineral Molecules (cont'd)

(Femic Group)

Acmite (ac)		$Na_2O . Fe_2O_3 . 4SiO_2$
Sodium metasilicate (ns)		$Na_2O . SiO_2$
Potassium metasilicate (ks)	P......	$K_2O . SiO_2$
Diopside (di)		$CaO . (Mg, Fe)O . 2SiO_2$
Wollastonite (wo)		$CaO . SiO_2$
Hypersthene (hy)		$(Mg, Fe)O . SiO_2$
Olivine (ol)	O........	$2(Mg, Fe)O . SiO_2$
Calcium orthosilicate (cs)		$2CaO . SiO_2$
Magnetite (mt)		$FeO . Fe_2O_3$
Chromite (cm)	H	$FeO . Cr_2O_3$
Hematite (hm)		Fe_2O_3
Ilmenite (il)	M...........	$FeO . TiO_2$
Titanite (tn)		$CaO . TiO_2 . SiO_2$
Perofskite (pf)	T	$CaO . TiO_2$
Rutile (ru)		TiO_2
Apatite (ap)		$3(3CaO . P_2O_5) . CaF_2$
Fluorite (fr)	A................	CaF_2
Pyrite (pr)		FeS_2
Calcite (cc)		$CaO . CO_2$

The Calculation[1]

In the following, the word "amount" should always be understood to mean the molecular number obtained by dividing the percentage weight of the constituent by its molecular weight.

1. The molecular number (amount) of each constituent is determined by reference to a table of molecular numbers. If the result is less than 0.002 it may be neglected.

---

[1] The rules have been slightly condensed from those given by Washington. The formulas have been solved once for all, so that the values for x, y and z may be obtained directly without combining equations, thus greatly simplifying the calculation.

2. The amounts of MnO and NiO are to be added to that of FeO, and those of BaO and SrO to that of CaO.

3a. An amount of CaO equal to 3.33 that of P_2O_5 (or 3.00 P_2O_5 and 0.33F, if the latter is present) is allotted for apatite.

3b. An amount of Na_2O equal to that of Cl_2 is allotted for halite.

3c. An amount of Na_2O equal to that of the SO_3 is allotted for thenardite. It must be remembered here that the SO_3 stated in the analysis often really represents the S of pyrite, so that rule 3c is applicable only when the rock contains minerals of the hauynite group.

3d. An amount of FeO equal to half that of S (or the S of erroneously stated SO_3 as above) is allotted for pyrite.

3e. An amount of FeO equal to that of the Cr_2O_3 is allotted for chromite.

3f. An amount of FeO equal to that of the TiO_2 is allotted for ilmenite. If there is an excess of TiO_2, an equal amount of CaO is to be allotted to it for provisional titanite, but only after the allotment of CaO to Al_2O_3 for anorthite (Rule 4d). If there is still an excess of TiO_2 it is calculated as rutile.

3g. An amount of CaO equal to half that of the remaining F is allotted for fluorite.

3h. If the rock is not decomposed and contains cancrinite, an amount of Na_2O equal to that of the CO_2 is allotted for sodium carbonate, which is to be considered as salic. If the rock contains calcite, an amount of CaO equal to that of the CO_2 is allotted for calcite. If the modal calcite is primary, the normative calcite molecule is to be regarded as femic; if the modal calcite is secondary, the calculated calcite molecule is to be disregarded as not forming part of the norm.

3i. Set aside the ZrO_2 for zircon.

4a. An amount of Al_2O_3 equal to that of the K_2O is allotted for provisional orthoclase.

4b. If there is an excess of K_2O over Al_2O_3 (an excess extremely rare), it is calculated as potassium metasilicate. For the Na_2O see Rules 5a and 5b.

4c. An excess of Al_2O_3 over the K_2O is allotted to an equal amount of remaining Na_2O for provisional albite. If there is insufficient Al_2O_3, see Rule 4g.

4d. If there is an excess of Al_2O_3 over the $K_2O + Na_2O$ used in 4a and 4c, it is allotted to an equal amount of remaining CaO for anorthite.

4e. If there is an excess of Al_2O_3 over this CaO, it is calculated as corundum.

4f. If there is an excess of CaO over the Al_2O_3 of 4d, it is femic and reserved for diopside and wollastonite (see Rules 7a and 7b).

4g. If in 4c there is an excess of Na_2O over Al_2O_3, it is to be reserved for acmite and possibly for sodium metasilicate (see Rules 5a and 5b). There is then no anorthite in the norm.

5a. To an amount of Fe_2O_3 equal to that of the excess of Na_2O over Al_2O_3 (see Rule 4g) is allotted an equal amount of Na_2O for acmite.

5b. If there is still an excess of Na_2O over Fe_2O_3 (a rare excess), it is calculated as sodium metasilicate.

5c. If, as usually happens, there is an excess of Fe_2O_3 over remaining Na_2O, it is assigned to magnetite, an equal amount of FeO being allotted to it out of what remains from the formation of pyrite, chromite, and ilmenite (see Rules 3d, 3e, 3f).

5d. If there is still an excess of Fe_2O_3, it is calculated as hematite.

6. All the MgO and the FeO remaining from the previous allotments (see Rules 3d, 3e, 3f, and 5c) are added together and their relative proportions are ascertained (most easily by the use of a slide rule).

7a. To the amount of CaO remaining after allotment in Rule 4d is allotted provisionally an equal amount of MgO + FeO to form diopside, the relative proportions of these two, as they occur in the remainder, being preserved.

7b. If there is an excess of CaO , it is reserved for provisional wollastonite.

7c. If there is an excess of MgO+ FeO over that needed for diopside (7a), it is reserved for provisional hypersthene.

All the oxides except SiO_2 have now been assigned to actual or provisional mineral molecules and we have next to consider the distribution of the silica.

8a. Allot the necessary amount of silica to ZrO_2 to form zircon (Rule 3i, 1:1), to CaO to form titanite (Rule 3f, 1:1), to excess Na_2O to form acmite (Rule 5a, 4:1), to excess K_2O and Na_2O to form potassium and sodium metasilicates (Rules 4b, 5b, 1:1), to K_2O for provisional orthoclase (Rule 4a, 6:1), to Na_2O for provisional albite (Rule 4c, 6:1), to CaO for provisional anorthite (Rule 4d, 2:1), to CaO+ (Mg, Fe)O for diopside (Rule 7a, 1:1), to excess CaO for wollastonite (Rule 7b, 1:1), and to (Mg, Fe)O for hypersthene (Rule 7c, 1:1).

The amounts of silica so assigned are subtracted from the total silica.

8b. If there is an excess of SiO_2, as there commonly is, it is calculated as quartz.

8c. If there is a deficiency of silica in 8a, the SiO_2 allotted to hypersthene (Rule 7c) is subtracted from the general sum of 8a and the remainder subtracted from the total SiO_2. If there is here an excess of SiO_2 more than enough to equal half the amount of (Mg, Fe)O of Rule 7c, it is allotted to the (Mg, Fe)O of 7c to form hypersthene and olivine, and is distributed according to equations (1) and (2):

Let x = the number of hypersthene molecules, y = the number of olivine molecules, M = the amount of available (Mg, Fe)O, S = the amount of available SiO_2; then

$$x = 2S - M, \qquad (1)$$

$$y = M - x. \qquad (2)$$

In this operation the relative proportions of MgO and FeO determined in Rule 6 and used in forming diopside (Rule 7a) are to be preserved. The fixed and

provisional molecules of Rule 8a are calculated into their percentage weights.

If there is not enough silica to equal half the amount of $(Mg, Fe)O$ of Rule 7c, all the $(Mg, Fe)O$ of Rule 7c is calculated as olivine, SiO_2 equal to half its amount being assigned to it.

8d. If there is a deficiency of SiO_2 in 8c, the SiO_2 allotted to titanite (3f) is subtracted from the general sum of 8a, and the CaO and TiO_2 are calculated as perofskite $(CaO \cdot TiO_2)$.

8e. The sum of the SiO_2 needed to form the molecules of 8a is deducted from the total SiO_2, except that olivine is substituted for hypersthene and perofskite for titanite, and that albite is not included. If there is an excess of more than twice (and, of course, less than six times) that of the Na_2O for the provisional albite of 8a, this is distributed between albite and nephelite according to equations (3) and (4). If the excess is less than twice the Na_2O, it is taken care of in Rule 8f.

Let x = the number of albite molecules, y = the number of nephelite molecules, N = the amount of available Na_2O, S = the amount of available SiO_2; then

$$x = \frac{S - 2N}{4} \quad , \qquad (3)$$

$$y = N - x \quad . \qquad (4)$$

8f. If there is still a deficiency of SiO_2 – that is, in 8e, not enough to equal twice the amount of available Na_2O – all this Na_2O is allotted to nephelite and the K_2O is distributed between orthoclase and leucite as follows: The sum of the SiO_2 needed for the molecules in 8a is subtracted from the total SiO_2, olivine being substituted for hypersthene, perofskite for titanite, and nephelite for albite, orthoclase being disregarded. If there is an excess of more than four times (and, of course, less than six times) that of K_2O, it is distributed between orthoclase and leucite according to equations (5) and (6). If the excess is less than four times the K_2O, it is taken care of in Rule 8g.

Let x = the number of orthoclase molecules, y = the number of leucite molecules, K = the amount of available K_2O, S = the amount of available SiO_2; then

$$x = \frac{S - 4K}{2} \quad , \tag{5}$$

$$y = K - z \quad . \tag{6}$$

8g. If there is still a deficiency of SiO_2 — that is, in 8f, not enough to equal four times the amount of K_2O — we have to distribute the CaO of wollastonite and diopside between these two and calcium orthosilicate, and the (Mg, Fe)O of diopside between diopside and olivine, according to available SiO_2. There are two possible cases.

The most common case is that in which there is no wollastonite or its amount is insufficient to satisfy the deficiency in SiO_2. Here, after allotting SiO_2 to form leucite (from all the K_2O), nephelite, anorthite, acmite, and olivine of Rule 8c, and possibly zircon and sodium metasilicate, the amount thus used is deducted from the total SiO_2, the residue being the available silica.

Let x = the number of new diopside molecules, y = the number of new olivine molecules, z = the number of calcium orthosilicate molecules, S = the amount of available SiO_2, M = the amount of (Mg, Fe)O (of provisional diopside), C = the amount of CaO of provisional diopside and wollastonite; then

$$x = \frac{2S - M - C}{2} \quad , \tag{7}$$

$$y = \frac{M - x}{2} \quad , \tag{8}$$

$$z = \frac{C - x}{2} \quad . \tag{9}$$

In these three equations x = half the number of SiO_2 molecules in diopside, y = the number of SiO_2 molecules in olivine, and z = the number of SiO_2 molecules in calcium orthosilicate.

If there are less than half as many molecules of silica as the sum of the CaO·(Fe, Mg)O of provisional diopside and olivine, use Rule 8h.

In the second case, where there is sufficient tentative wollastonite to meet the deficiency of SiO_2, the total amount of SiO_2 in the rock is subtracted from the sum of the SiO_2 which has been allotted to leucite, nephelite, anorthite, acmite, diopside, olivine, and to tentative wollastonite. The deficit is the number of molecules of necessary calcium orthosilicate, and also the amount of SiO_2 to be assigned to it. This requires twice as much CaO. The rest of the CaO remains in wollastonite and takes an equal amount of SiO_2, while the diopside remains unchanged.

8h. If, as may very rarely happen, there is not even enough SiO_2 to form leucite, we must assume the presence of the kaliophilite molecule in the norm and distribute the K_2O between this and leucite. Diopside and wollastonite fall out, the CaO contained in them being used as calcium orthosilicate and the (Fe, Mg)O as olivine. The sum of the SiO_2 needed for nephelite, anorthite, acmite, sodium metasilicate, olivine, calcium orthosilicate, and zircon is subtracted from the total SiO_2, and the amounts of leucite and kaliophilite are calculated according to equations (10) and (11).

Let x = the number of leucite molecules, y = the number of kaliophilite molecules, K = the amount of K_2O, S = the amount of available SiO_2; then

$$x = \frac{S-2K}{2} \quad , \tag{10}$$

$$y = \frac{4K-S}{2} \quad . \tag{11}$$

9. Having adjusted the amounts of the SiO_2 and all the other constituents between the fixed molecules and those with differing ratios of SiO_2 (the provisional becoming the actual molecules), they are calculated into the percentage weights of the mineral molecules of the norm by the use of tables.

10. The position of the magma in the classification is now to be determined, the class by the ratio of sal. to fem., the order by the ratio of quartz to feldspar or lenad to feldspar in Classes I, II, and III, and by P + O to M in Classes IV and V, etc., etc.

(Johannsen, A descriptive petrography of igneous rocks, 88 - 92)

Chapter 3

THE INSTRUMENTATION PACKAGE AND ITS LUNAR ENVIRONMENT

THE INSTRUMENTATION PACKAGE AND ITS LUNAR ENVIRONMENT

Instrumentation Package – General Considerations

The maximum allowable weight of the complete lunar analyzer has not been decided. It appears that it is very unlikely to be below 25 lb. or above 250 lb. and that a suitable design target would be in the range 25 - 50 lb.

The stray magnetic field produced by the analyzer in the spacecraft after landing on the Moon has to be kept to about 0.1γ, which necessitates either the use of a completely non-magnetic analyzer, or very careful shielding. This requirement apparently results from expectations that a magnetometer experiment is likely to be carried on the same lunar shot. If no magnetometer were present, the allowable stray fields would of course be much larger.

Power consumption must obviously be minimized; however, it must be assumed that a power consumption several times greater than that of existing flyable gas-analysis mass spectrometers could be tolerated for short periods of time, such as might be required to analyze one small sample of the lunar crust.

Physical strength and sensitivity to impact damage of the lunar analyzer must clearly be not inferior to that of existing flyable instruments, and preferably superior.

Protection must be provided, by means of a suitable housing and baffles, for exclusion of falling dust from the critical parts of the lunar analyzer, and for the prevention of accumulation of any dust which does enter, by means of suitable "drain holes". The extent of the dust problem is unknown, but it is probable that the disturbance involved in the spacecraft landing, in the occasional impacts of micrometeorites in the locality, and in the possible intermittent release of sub-surface gases may result in a fairly substantial dust fall during the life of the instrument package. If the dust is electrically charged, an almost completely enclosed instrument may be required.

In order to obtain an accurate sampling of the lunar atmosphere, which is thought to exert a pressure of 10^{-11} to 10^{-14} torr, it is important that the ion source

be comparatively open to the lunar environment and that it be thoroughly outgassed by the time of analysis. The complete analyzer head should be kept in an evacuated environment until it leaves the Earth's atmosphere.

Orientation of the ion source after landing is important, so that the gases sampled by it may be of lunar origin rather than the outgassing products of the spacecraft or of the landing area (which will have been exposed to retro-rocket exhausts).

In order to properly analyze the lunar atmosphere the ion source must therefore be comparatively open to the lunar environment while at the same time being protected from dust-fall and from "seeing" the spacecraft and landing area. In order to establish the severity of the outgassing effects from spacecraft and landing area, it would be useful to arrange a controllable or automatically timed shutter on the ion source so that these normally unwanted molecular beams could be admitted temporarily.

The mechanical problems of obtaining solid samples and transporting them into the ion source region are not required to be included in this study.

TEMPERATURE RANGE AT THE LUNAR SURFACE

Pettit and Nicholson (1) measured the heat radiation from various regions of the Moon and calculated the corresponding surface temperature. For the full Moon they determined the following temperatures at the indicated fractional distances from the center to the limb; 134° C at 0.0 radius (the subsolar point), 122° C at 0.5 radius, 102° C at 0.75 radius, 77° C at 0.9 radius, and 67° C close to the limb. When the temperature of the subsolar point was measured at the half phases a surprise resulted, for it was only 81° C. The great roughness of the surface must account for this difference and, thus, we must be careful in assigning a unique temperature to any particular region on the Moon. During the long lunar night the temperature is fairly constant at about -153° C. During a lunar eclipse Pettit (2) observed that at a point along the path of the center of the earth's shadow the temperature dropped from a pre-eclipse value of 69° C to −63° C at the beginning of totality one hour later, and continued to drop to − 121° C during the total phase of the eclipse.

The highest temperature is approximately the equilibrium temperature, 119° C, of a black plane at the same distance from the sun and illuminated by sunlight and radiating from only its front side. For comparison the equilibrium temperature of a black sphere illuminated by sunlight would be 4° C. If, in addition, the black sphere is just above the lunar surface and so is illuminated by sunlight on the sunward side and is illuminated by the radiation from the surrounding lunar surface at an average temperature of about 100° C on the lower side, it will have a temperature intermediate between the black sphere temperature, 4° C, and the average temperature of the surrounding lunar surface, about 100° C.

The actual temperature of an object near the lunar surface can be modified considerably from the above equilibrium black body values by properly arranging the absorbing and emissive properties of its surface and, of course, for any

element contained inside the object by the use of insulation and a heat source. Much research and practical experience in the use of such technics has already been involved in the space research program. Recently, also, Butler and Jenkins (3) have calculated the temperature of meteoroids with different radiative characteristics.

REFERENCES

1. "Lunar Radiation and Temperature" by Pettit and Nicholson, Astrophys. J. 71, 102 (1930).

2. "Radiation Measurements on the Eclipsed Moon" by Pettit, Astrophys. J. 91, 408 (1940).

3. "Temperature of an Iron Meteoroid in Space" by Butler and Jenkins, Science 142, 1567 (Dec. 20, 1963).

THE RADIATION AT THE LUNAR SURFACE

I. The Sources of Radiation at the Lunar Surface

To predict the quality and quantity of radiation at the lunar surface, it is necessary to consider each of the sources that contribute to this radiation and to estimate the intensity of each contribution. This requires that we use the appropriate existing measurements of the radiation from the various sources and properly infer how they will contribute to the radiation field at the lunar surface. But unfortunately, the existing measurements do not adequately specify all aspects of these radiations, e.g., the energy distribution, intensity variations in space and time, etc., and they do not give us a complete knowledge of the interactions of these radiations with matter. In addition, it is necessary to adopt models for the composition and structure of the lunar surface and these can be inferred only poorly from our present knowledge of the moon. For these reasons any quantitative predictions of the amount of radiation at the lunar surface are subject to large error. In addition, the amount of radiation in a particular volume considered can be altered considerably by the presence of nearby mass, particularly in the form of shielding.

Since our interest here is in the total amount of ionization produced, including ionization produced at appreciable depths (say greater than 0.1 mm), we need not consider electromagnetic radiation of wavelengths longer than the soft x-ray limit nor particle radiation with energy less than about one Mev. On the other hand, we must consider any radiation which does not produce much ionization itself but which is capable of penetrating deeply into materials and producing secondary particles that are strongly ionizing. In situations where we lack the necessary detailed information, we will need to rely, as much as possible, on existing measurements of the total ionization produced by all components of the radiation from a particular source.

We need to consider the radiation at the lunar surface originating from the

following sources:

    A. Primary cosmic radiation.

    B. Primary gamma radiation.

    C. Solar radiation.

        1. Quiet sun

        2. Disturbed sun

    D. Secondary cosmic radiation.

        1. Normal radiation

        2. High energy events

    E. Induced radioactivities in lunar material.

    F. Natural radioactivities in lunar material.

II. <u>The Quantity of Radiation.</u>

    A. <u>The primary cosmic radiation.</u>

The intensity of the primary cosmic radiation at the lunar surface is expected to be similar to the intensity at the top of the earth's atmosphere with a due allowance for the low energy cut-off produced by the earth's magnetic field. The omnidirectional primary cosmic ray intensity was recently given (1, p. 84) as 2.1 ± 0.2 cm^{-2} sec^{-1} which corresponds to an intensity of .33 cm^{-2} sec^{-1} sr^{-1}. For a cm^2 lying horizontally on the lunar surface and thus completely shielded from the lower hemisphere by the moon we expect 2.1 primary cosmic ray particles to traverse the cm^2 each second.

Most of the primary cosmic radiation consists of protons. About 10% of the flux is $\propto$ -particles and 1 to 2% consists of heavier nuclei (1, p. 88). Since the number of cosmic ray particles decreases exponentially with increasing energy, the number of primaries that produce a particular effect is strongly dependent on the low energy threshold required to produce the effect. Recent experiments indicate that in fact there is a large number of particles with energy less than 600

Mev. but considerable uncertainty still exist about the number of particles and their energy distribution (5, 6, 7).

B. Primary gamma-radiation (γ)

The intensity of the primary γ-radiation has recently been measured by several investigators (2, 3, 4). We can adopt as representative of this work the value 2×10^{-3} γ-rays cm^{-2} sec^{-1} sr^{-1}. If we integrate over the upward hemisphere we obtain the number of such primary γ-rays that traverse a cm^2 lying on the lunar surface in one second, i.e., 1×10^{-2} γ-rays cm^{-2} sec^{-1}. (But in the work reported by Duthie et al (4) the detector had a γ-ray energy threshold of 60 Mev.) Thus it appears that the intensity of the primary γ-radiation incident on a cm^2 lying on the lunar surface will be only a small fraction of that of the secondary γ-radiation produced by the interaction of primary cosmic radiation with the lunar material. Therefore the effect of primary γ-radiation at the lunar surface can be neglected.

C. Solar Radiation

1. Solar gamma-radiation

Detectors that were sensitive to γ-rays with an energy greater than 200 Mev. indicated an upper limit of γ-ray flux from the sun of 8×10^{-3} photons cm^{-2} sec^{-1} (8). While this number may be increased during the time of flares, we nevertheless expect the contribution to the radiation at the lunar surface from solar gamma rays to be negligible.

2. Solar x-rays

Measurements of the x-rays in the range $8\text{Å} < \lambda < 100\text{Å}$ indicate a flux density of about 0.1 erg cm^{-2} sec^{-1} (7). The energy distribution of these x-rays is approximately represented by a Planckian distribution for $700,000°$ K. During the times of solar-flares there is a marked increase in the amount of this radiation and also there is a measurable amount of more energetic

x-rays: during flares, x-rays with energy greater than 20 keV have a flux of about 4.5 x 10^{-6} erg cm^{-2} sec^{-1} and detectors with responses in the range 2 - 8 $\overset{o}{A}$ and 8 - 20 $\overset{o}{A}$ were saturated (10).

3. Solar particle radiation

Measurements of the cosmic radiation generally include the particles of solar origin. A large fraction of the particles at the low energy end of the cosmic-ray spectrum are attributed to a solar origin. Since it is in this region that cosmic-ray particles are most abundant, we see that the sun plays an important role in determining the amount of radiation at the lunar surface. Further, the solar component is variable with the period of the sun's rotation and with the period of the sun spot cycle. Recent experiments indicate that a large number of particles with energy less than 600 Mev exists, but considerable uncertainty still exists about their number and energy distribution (5, 6, 7).

During times of solar flares, particles with energies from a few million to a few billion electron volts are emitted by the sun. While the flares occur only at relatively rare intervals and are of short duration, it has been found that the radiation emitted during these short flare periods may greatly exceed all of that emitted during long periods between flares. As an example, during seven flares between 1956 and 1961 the radiation dose under 1 g cm^{-2} of water shielding at the earth's distance exceeded 100 rads (11). Further, during the International Geophysical Year 10 to 15 particle-producing flares a year were observed. For comparison the galactic cosmic rays contribute a yearly dose of between 5 to 15 rads. Since the solar flare particles arrive almost isotropically at the earth for several days after the visible flare, it is apparent that they will make an important contribution to the radiation at the lunar surface. The exposure to such particles can be substantially reduced by confining observations to times of sunspot mimimum, by making use of "solar weather predictions" and, since these particles

include many of low energy, by modest amounts of shielding.

D. Secondary cosmic radiation

Secondary cosmic radiation makes an important contribution to the radiation at the lunar surface. This radiation consists of ionizing particles such as electrons, protons, helium and other nuclei, neutral and lightly ionizing particles such as neutrons and mesons, and γ-radiation. The amount of secondary cosmic radiation, produced in any shielding or structural material (such as a lunar probe) above the lunar surface region considered can be calculated if the composition, amount and geometry of the probe material is specified. However, the amount of secondary radiation coming from the lunar surface material itself cannot be calculated satisfactorily from our present knowledge. This difficulty arises for two reasons: the composition and structure of the lunar material is not known and the lunar material is below the region considered. Since in the interaction of a cosmic ray primary with matter a large fraction of the secondary radiation is emitted in a cone oriented in the same direction as the primary, careful allowance for this must be made in the calculations. The radiation that is emitted in the backward direction is often referred to as the "albedo radiation". Calculations have been made of the albedo neutron radiation expected from the lunar surface, and for a basaltic composition of the moon the calculated value is 0.26 neutrons cm^{-2} sec^{-1} (12); and this flux may increase appreciably during solar flares. It appears that the most important contribution to the secondary radiation will be made by primaries striking the surface of the moon at low angles around the region considered. For such low-angle primaries some of the forward oriented secondaries will come up out of the lunar surface and traverse the region considered. If we assume that the primary radiation is isotropic over the upward hemisphere, we notice that one fourth of the incident radiation comes from directions that are closer than 15° to the horizontal plane. It is also

necessary to consider the contribution produced by the occasional high energy events.

At present, we must work with models of the lunar surface - model compositions such as those outlined elsewhere in this report, and model surface relief structures and textures. Careful and detailed calculations of various model lunar probe-lunar surface-lunar composition systems will be necessary to provide a basis for accurately estimating the amount and composition of secondary cosmic radiation produced from lunar and probe materials reaching the sensitive regions of the probe. The single example of a model moon calculation given above (0.26 neutrons $\cdot$ cm^{-2} sec^{-1} for quiet sun periods) indicates that such secondary radiation presents a serious problem both to manned expeditions and unmanned probe experiments, which must be studied in detail in advance if successful exploration of the lunar surface is to be accomplished.

E. Induced radioactivities in lunar material

Although the induced radioactivies in the lunar material are caused by the action of cosmic radiation, they are best treated separately from the usual secondary radiation. These induced radioactivities will make a contribution to the particle and gamma radiation at the lunar surface. The intensities of such radiation from each of the different radioactive nuclei will depend on the equilibrium amount of each nucleus and therefore on the cosmic ray intensity integrated over a few half lives of the nucleus. Many of these radioactive nuclei may have half lives sufficiently long so that the important, though occasional, high energy events and flares determine the equilibrium amounts present and thus also the intensity of the radiation from their decay. The observations of cosmic-ray induced radioactivities in meteorites will serve as a good guide in estimating the amount of radiation from this source (13, 14, 15). Again, the actual activities present will depend on the actual composition of the lunar surface region under considera-

tion, and again, detailed calculations based on model composition would be necessary to make a proper estimate of these activities.

F. Natural radioactivities in lunar material

We expect that uranium, thorium and potassium will be the most important naturally radioactive elements in the lunar material. At present it appears that the abundances of these elements in the lunar material will be similar to their abundances in terrestrial igneous rocks, perhaps of basaltic type, or chondritic meteorites. But since these abundances are low and since the particle and gamma radiations produced have relatively short ranges, this source is not expected to make an important contribution to the radiation above the lunar surface, compared to the other sources.

REFERENCES

1. "Cosmic Rays" by A. W. Wolfendale, G. Newnes Lmt. 1963.

2. "Search for High-Energy Cosmic Gamma Rays" by Cline, Phys. Rev. Let., 7, 109 (1961).

3. "Search for Primary Cosmic Gamma Rays with Satellite Explorer XI", by Kraushaar and Clark, Phys. Rev. Let. 9, 106 (1962).

4. "γ-Rays at High Altitudes" by Duthie et al., Phys. Rev. Let. 10, 344 (1963).

5. "Progress in Elementary Particle and Cosmic Ray Physics", article by Webber editors Wilson and Wouthuysen, North Holland, Amsterdam, 1962.

6. "Report of Enrico Fermi Institute for Nuclear Studies", EFINS 61-43, by Vogt, 1961.

7. "Mariner II: Preliminary Reports on Measurements of Venus", by Frank et al, Science 139, 905 (1963).

8. "An Attempt to Detect Energetic Gamma Radiation from the Sun", by Danielson, J. Geophys. Res. 65, 2055 (1960).

9. "The Solar X-Ray Spectrum and the Density of the Upper Atmosphere" by Byran et al., J. Geophys. Res. 61, 251 (1956).

10. "Measurements Made of High-Energy X-Rays Accompanying Three Class 2$^+$ Solar Flares" by Chubb et al, J. Geophys. Res. 65, 1831 (1960).

11. "Radiation Hazard in Space from Solar Particles" by Freier and Webber, Science 142, 1587 (December 20, 1963).

12. "Estimate of Neutron Albedo on the Moon's Surface Resulting from Cosmic Radiation" by Rao, Science 141, 530 (1963).

13. "The Ehole Meteorite, Its Acquisition and Its Radioactivity", by Fireman, J. Geophys. Res. 67, 2592 (1962).

14. "Cosmic Ray Induced Radioactivity in a Fresh Meteorite" by Anders et al, J. Geophys. Res. 65, 2471 (1960).

15. "Proton Bombardment of a Simulated Iron Meteorite" by Shedlovsky and Kohman, J. Geophys. Res. 67, 3598 (1962).

INTERACTION OF RADIATION AT LUNAR SURFACE
WITH ELECTRONIC COMPONENTS

A reservoir of experience on the interaction of radiation and other unique elements of the space environment, gained from satellite experiments and deep space probes as well as laboratory experiments, already exists within the National Aeronautics and Space Administration and its contractors. Much of this experience can be directly applied to the case of an electronic unit situated on the lunar surface. However, it must be recognized that this environment is different in many details from the space environment.

An important difference pointed out in the preceding discussion is the importance of secondary radiation in the vicinity of the lunar surface, arising from reactions of primaries with surface materials. Because of this secondary radiation, electronic components in a lunar surface probe will be exposed to a stronger radiation flux and one of different composition from that experienced by a probe in space or in circumterrestrial or circumlunar orbit. This requires that new, stringent standards of performance be developed for the electronic components that are to be exposed to lunar surface conditions, on the basis of more accurate estimates of the actual lunar surface radiation flux − which, as is recommended above, still apparently need to be developed. It is therefore presently not possible for us to attempt to define the effects of the lunar radiation environment on electronic components with exactitude; nor was this an object of this preliminary study. It is an area in which additional work must be done.

Nevertheless, some comments on one problem that may prove to be important, depending on the actual radiation level and composition, may be useful. Any electronic system intended for space use will almost certainly be designed around semiconductor devices. It is very probable that the primary effect of radiation exposure of such devices will be to produce a cutoff collector current in excess of that

encountered in normal transistor operation. It is likely that thermal runaway induced by this means will become an important threat to the life of the device well before actual radiation damage is suffered by the material itself.

It is well known that a transistor draws a small cutoff collector current I_{CO} even when the base current is zero due to minority charge carriers originating from the thermal production of hole-electron pairs. Since this current flows through the base-emitter junction as well as the collector-base junction, it constitutes a base current which is non-zero even with the base lead open-circuited. The total collector current under such conditions is then

$$I_C = (\beta + 1) I_{CO}$$

where β is the common emitter forward current transfer ratio. If in addition a base current I_B is made to flow in the base lead, the total collector current becomes

$$I_C = \beta(I_B + I_{CO}) + I_{CO} \qquad .$$

Thermal runaway occurs when this current results in sufficient heating of the transistor to raise I_{CO} by the thermal generation of more minority charge carriers so that I_C is raised, raising the temperature still further. Obviously, a measure of the susceptibility of a transistor circuit to thermal runaway is the rate of change of I_C with I_{CO}. Thus a stability factor

$$F = \frac{\partial I_C}{\partial I_{CO}}$$

is defined and should be made as small as possible for good stability. Note that in a so-called "fixed bias" circuit in which I_B is a constant, $F = \beta + 1$ and is thus very large for a high gain transistor. A fixed bias circuit is thus highly unstable, and other circuits have been developed which essentially make I_B depend on I_C with the aim of making the quantity $(I_B + I_{CO})$ constant independent of I_{CO}. Normally, the resulting stability factor of unity is not achieved in practice as a large sacrifice in stage gain usually results, but $F = 6$ is commonly taken as a sufficiently small value.

Upon exposure of a transistor to radiation, it is likely that the radiant flux will produce further hole-electron pairs. Let P be the probability of producing such a pair per unit time. Then in time interval dt, Pdt minority charge carriers will be produced resulting in an additional cutoff collector current

$$I_{rCO} = eP$$

due to the radiation (where e is the electronic charge). The total collector current with no base current will then be

$$I_C = (\beta + 1)(I_{CO} + I_{rCO}) \quad .$$

It is necessary to take this total cutoff collector current into account when designing semiconductor systems for use in space. Sufficient cooling must be provided so that the extra dissipation occasioned by this current does not result in an excessive temperature rise, and transistor circuits must be designed so that the operating point does not shift excessively in response to radiation exposure (i.e., attention must be paid to having small stability factors), and, in the case of diodes, in which $I_{CO} + I_{rCO}$ represents an undesirable reverse current, it must be ascertained that the circuits can tolerate the reverse currents which may arise in the expected radiation levels.

It seems probable to the writers that problems such as the above are under continuing study at N.A.S.A. and A.E.C. laboratories and by certain contractors. Thus, as soon as an accurate idea of the quantity and character of the lunar surface radiation flux has been developed, it will be possible to judge whether adequate studies of existing devices in comparable fluxes have already been made, and if so, to write component and shielding specifications forthwith. It would appear at present, however, that some additional environmental testing will be required on account of the unique radiation environment in which an analyzer stationed on the lunar surface will be expected to operate for extended periods.

Chapter 4

ION SOURCES

ION SOURCES

1 Electron Bombardment Sources

1A. Electron Bombardment Ionizers

The most widely used ion source in mass spectroscopy is the classical electron bombardment source (1). In this source the sample to be studied is introduced in the gaseous phase and a fraction of it is ionized by a beam of electrons of controlled energy. It has heretofore found application mainly in the routine compositional analysis of gases, liquids, and solids which have vapor pressures of more than 10^{-6} torr at inlet system temperatures of up to about 300° C. However, this source may also be used with low vapor pressure materials providing they are first vaporized. In fact two kinds of "source" are required — a means of vaporizing the solid or liquid sample (the vaporizer) and a means of ionizing the vapor (the ionizer). Sources such as the r-f spark perform both functions simultaneously. If the "classical" electron bombardment source is to be used, a separate vaporizer is required.

Some means of vaporizing solids (crucible, arc-image, laser) are discussed in later sections. The classical electron bombardment ionizers will not be discussed in detail as there are many thorough treatments in the literature. However, some less-well-known electron bombardment source types deserve mention in connection with the study of solids — these are sources which achieve ionization efficiencies markedly higher than can be achieved with the "classical" source.

Mass discrimination occurs in any type of electron bombardment source; but much data already exists on these discriminatory effects in the "classical" EB source, and so calibration of such sources is reasonably straightforward.

a. <u>Quadrupole lens sources</u>: C. Giese has constructed a quadrupole lens that takes electrons from a large-area cathode and focuses them into a high-intensity beam which intercepts the molecular beam to be studied (2). This ionizer is likely to be useful in many types of studies in which a high efficiency is essential because the molecular beam currents are very small, as they are almost certain to be in the case of lunar crust analysis.

b. <u>Oscillating electron sources</u>: Several authors have described electron bombardment ion sources in which a large increase in efficiency has been achieved by greatly increasing the average path length of an ionizing electron in the ion chamber. A source of this type described by H. Heil (3) is shown in Figure 3. Another source of the same general type, the Finkelstein source (4) is shown in Figure 4. In both sources, the combination of an axial magnetic field and suitable filament and/or electron "trap" potentials causes the electrons to describe spiral paths back and forth through the ionizing region many times before they are lost to the walls. The fraction of gas atoms ionized in the source is thereby greatly increased. The ions formed have, however, an energy spread of several electron volts compared to the ± 0.1 eV spread achievable in the classical electron bombardment ion source.

c. <u>Weiss Source</u>: Another type of high efficiency ion source has recently been developed by R. Weiss (5) for use as a molecular beam ionizer. In this source (Figure 5) electrical fields are so disposed as to form a virtual cathode composed of electrons. The molecular beam passes longitudinally through this electron cloud. The electron space charge is used to focus and accelerate the positive ions produced. An ionization efficiency of 1 in 40 for an argon molecular beam was achieved and efficiencies as high as 10% are expected from an improved version. The energy spread is dependent on design parameters; in the first model built it was of the order of 20 eV.
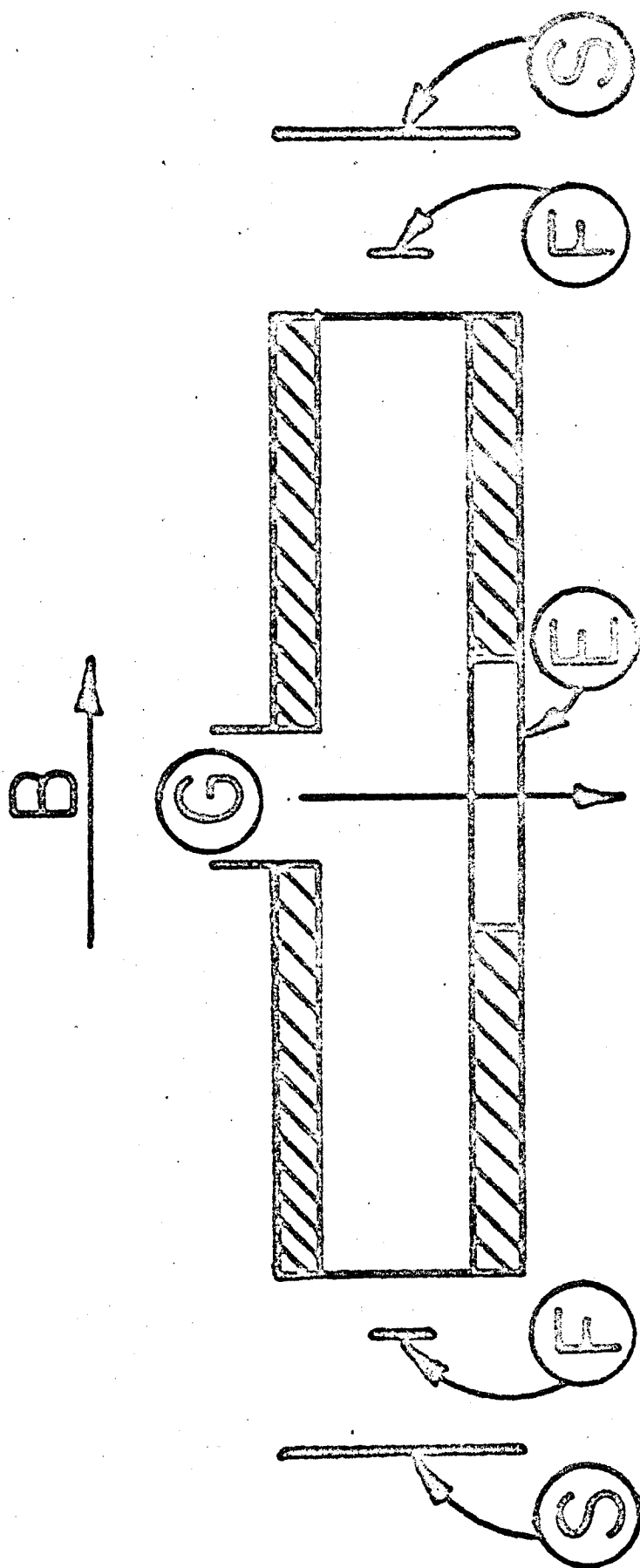
Figure 3

Cross-section of ion chamber of oscillating electron bombardment source of the type described by Heil F = filament, S = cathode screen, G = gas inlet, E = ion exit slit, and B shows direction of external magnetic field.

Figure 4. The ion bombardment source used in the Nuclide type DB-1 spectrometer. The ion source is the Finkelstein type, similar to that described by Nielsen.

Figure 5

High efficiency ion source for
molecular beams as suggested
by Weiss

1B. Vaporizers and Molecular Beam Sources

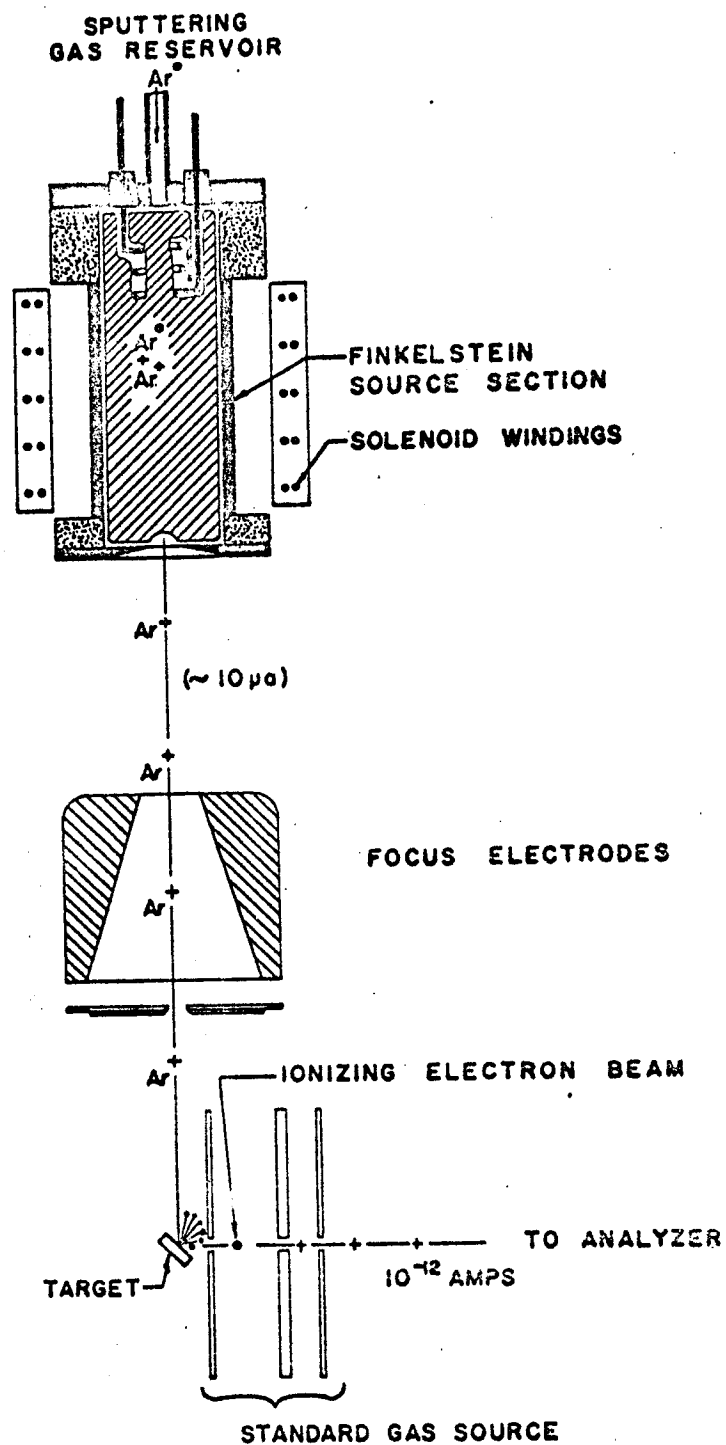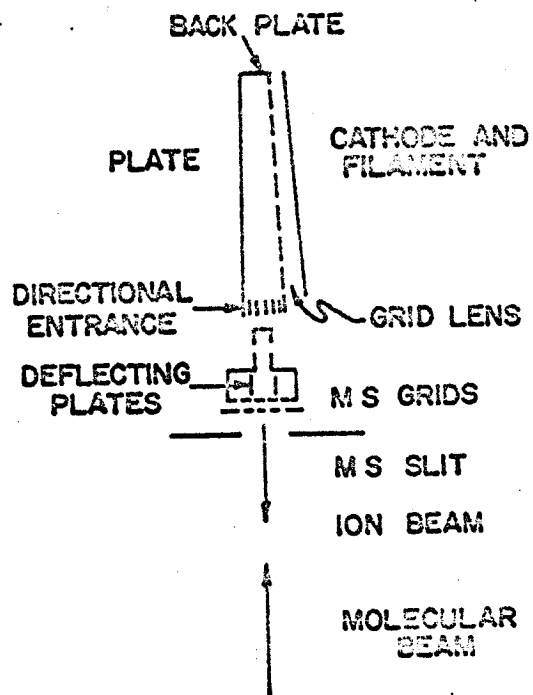a. Electron bombardment vaporizers: Even refractory metals and insulators can be vaporized by direct electron bombardment. Considerable ionization naturally also occurs. The ions can be suppressed, if necessary, and the neutrals passed into a separate ionization region. Alternatively, the ions could be analyzed directly if suitable account were taken of the effects of the very high electron energies required. The electron beam has to be carefully focused; a magnetic field is usually employed for this. Lakomskii (6) has successfully demonstrated the use of a pulsed, accurately focused electron beam for localized vaporization of ceramics and metals in a mass spectrometer ion source. Fig. 6 shows a small commercial electron bombardment vaporizer.

It might be expected that, with insulating samples in a very high vacuum, difficulties would appear as a result of charge buildup on the sample surface defocusing the electron beam. However, recent work (7) has shown that this problem is rather easily overcome by using sufficiently strong beam focusing. A small electron gun capable of vaporizing insulators such as glass and quartz has been successfully operated. The main difficulties are the high power consumption (several hundred watts of power are needed for samples in the 0.1 gm range) and the problem of removing heat from the beam collector. It appears likely that careful miniaturization could make possible a reduction in power consumption to the point where at least intermittent operation could be achieved in a lunar analyzer.

b. Laser source: Lasers have now been developed to the point where they can be used to weld refractory metals and to drill small-diameter (0.020") holes, even in diamonds (8). Some of them provide means of very intensely heating small sample areas in exceedingly short times. In the diamond experiment, surface temperatures of 5500° C were reached.

SAMPLE

ELECTRON EMITTER
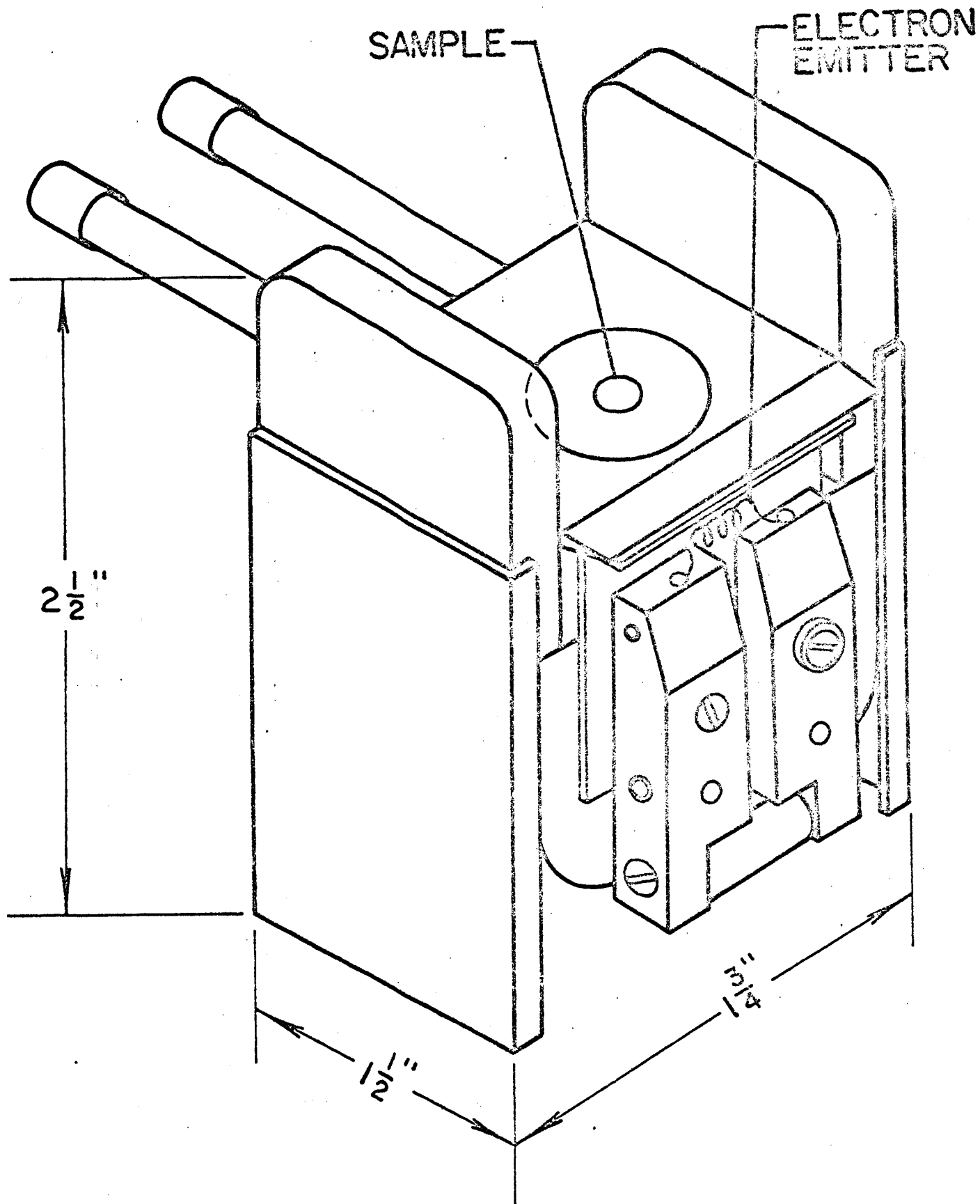
$2\frac{1}{2}$"

$\frac{3}{4}$"

$1\frac{1}{2}$"

Fig. 6. Varian Electron Bombardment Vaporizer

Pulsed lasers are available today which achieve light outputs above ten million watts. Single pulses of duration as short as ten millionths of a second and as long as one millisecond have been generated. Rather inexpensive devices can deliver as much as 20 joules of energy, which, when delivered in such short pulses, can vaporize a needle-sized hole through a piece of steel 1/32" thick. The laser beam can be focused to a 10 micron spot, using rather primitive techniques, and theoretically it should be possible to focus to a one micron spot.

Honig and Woolston (9) and Honig (10) have reported on the use of laser beams in conjunction with a mass spectrograph for the study of surfaces. They, as well as Lichtman and Ready (11), have observed laser-induced emission of electrons, ions and neutral atoms. The ions are apparently produced by thermal ionization. Neutral vapor species were detected by producing a low voltage arc discharge in the laser vapor plume and causing electron bombardment ionization to take place. Ion currents as large as 10^{-5} amperes were obtained, leading in some cases to space charge broadening of lines.

Presently available lasers have light outputs in the wave length range of about 25,000 A^{o} to 7,000 A^{o}. Thus, they have equivalent energies of up to about 2 eV. If devices operating in the 2000 A^{o} region and below can be developed, they will provide a means of direct photoionization in addition to vaporization and surface ionization.

Compared to the arc-image, laser heating appears to offer better temperature and location control, smaller spot areas, a more precise means of sampling in depth, and a less cumbersome apparatus. The possibility of using the device for "microprobe" studies appears to be very good.

c. Arc-Image: In arc-image heating, radiant energy is focused onto the sample by a system of mirrors. Temperatures of up to 4000° K may be

attained in spots of about one cm. in diameter (12). An electron-beam ionizer is required for vapor analysis.

The advantages of arc-image heating are that high temperatures can be achieved, contamination caused by an emitting filament is absent, non-conductors are easy to study, and the sample can be heated independently of its support. There are some disadvantages of this type of heating: as material evaporates the sampling point migrates and focusing may deteriorate, and thermodynamic equilibrium is not achieved – instead, free evaporation occurs – but of course, there is a class of experiments in which free evaporation is desirable. Still, the arc-image technique seems to offer a means of vaporizing all known materials at temperatures which can be made so high that element fractionation effects will be minimal. The technique may be especially useful in trace constituent studies of non-conductors, since the problem of contamination from the supporting metallic electrodes which are used to make possible r-f spark-source investigations of non-conductors (13), is absent with arc-image heating. Apparently, the arc-image source was first formally suggested by Goldfinger (14). At least two other laboratories are also investigating this type of source (15, 16   ).

Previous work on arc-image sources has mainly been done using parabolic or spherical mirrors to focus radiated energy from an electric arc onto the sample. Obviously an electric arc would have too high a power consumption for use in a lunar analyzer. However, the absence of an atmosphere and the lower gravitation forces on the moon suggest the possibility of imaging the sun's radiation onto the sample material. Since the heating would effectively be carried out in a vacuum, lower power concentrations would be required than is the case for solar furnaces on the earth. A sun-seeking mirror would of course be necessary.

d. <u>Crucible</u>: A crucible may be heated by any one of a variety of techniques – ohmic heating, electron bombardment, r-f induction, or even focused solar heating. It is then possible to study the molecules, atoms, and ions that are produced as a function of temperature. The usefulness of crucible-type vapor sources in trace constituent analysis is limited both because the inherent gas use efficiency is low and because the crucible may be a source of contamination. Nevertheless, in many cases, crucibles can be useful for such analyses. A special and very useful feature of crucible sources is that they are capable of delicate temperature control.

e. <u>Knudsen cell source</u>: Systems at equilibrium at high temperature can be studied with a special type of crucible, the Knudsen effusion cell (17). A modern Knudsen source is shown in Figure 7 . An electron beam is used to ionize neutral atoms and molecules emerging from the crucible. Equilibrium studies with temperatures as high as 2700° K have been made with such sources. Applications of the Knudsen cell technique in chemical physics have been discussed by Inghram and Drowart (17).

At temperatures above approximately 2500° K, operation of heated-crucible type sources becomes increasingly difficult. The reason for this are: mechanical instability due to thermal weakening, excessive power demand due to radiation losses, electrical breakdown due to pressure buildup caused by heating, and temperature control problems occurring as heat shields begin to radiate electrons. Above these temperatures it is desirable to employ other methods of heating the sample.

2. <u>The Ion Bombardment (Sputtering) Source</u>

When a solid is subjected to ion bombardment, some material is removed (or "sputtered") from its surface and, if the ion bombardment is con-

FINAL COLLIMATING SLIT

BEAM CENTERING PLATES

PRIMARY COLLIMATING PLATE

FOCUSING PLATE

DISCRIMINATING PLATES

DEFOCUSING PLATE

FILAMENT

FILAMENT MOUNTING PLATE

SHUTTER

RADIATION SHIELDS

CRUCIBLE

RADIATION SHIELDS

OVEN SUPPORT PLATES
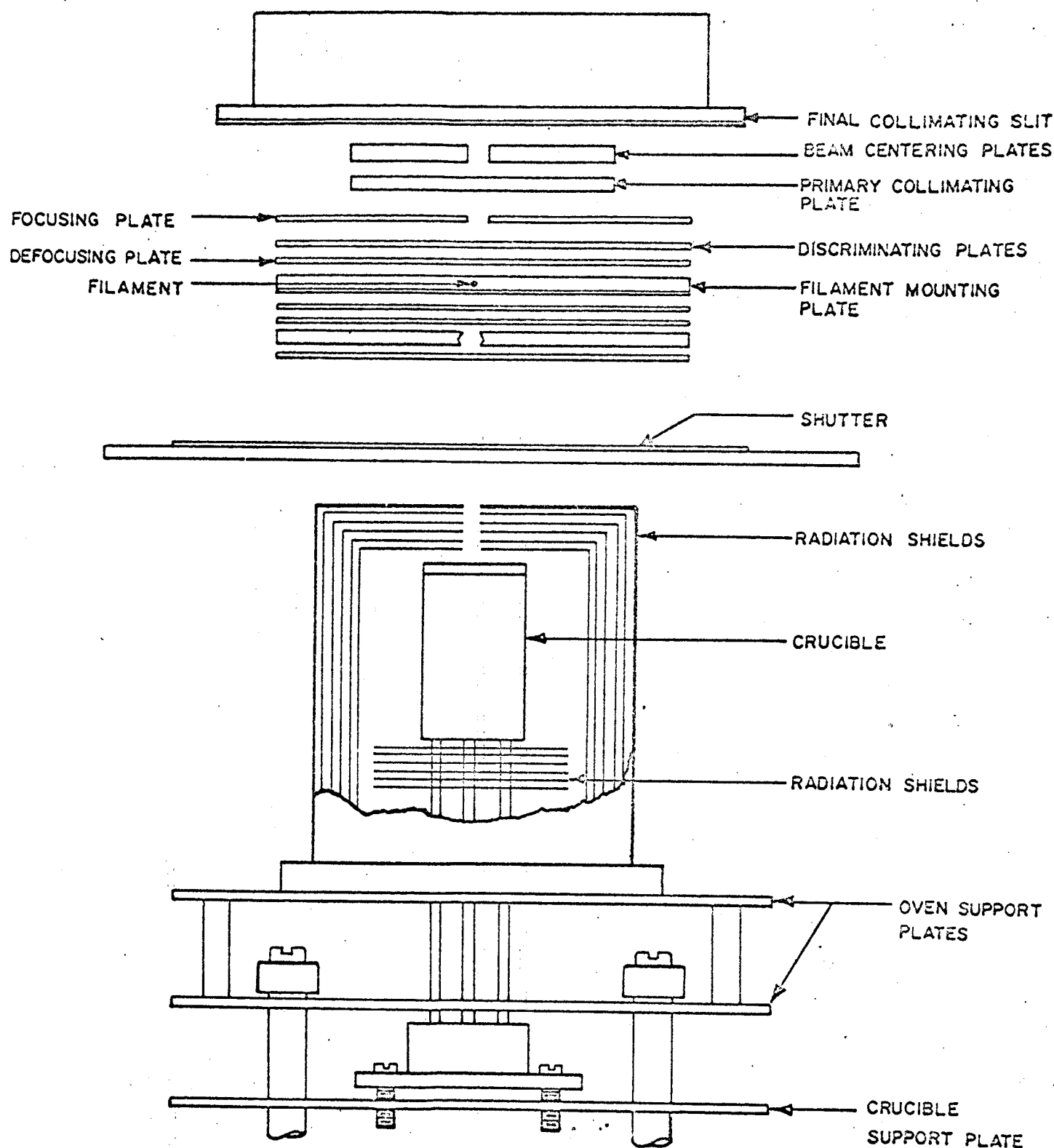
CRUCIBLE SUPPORT PLATE

Figure 7

A Knudsen effusion cell vapor source with ionizing electron gun;
Nuclide type HT-7. Studies of systems at equilibrium have been
made at temperatures up to 2700° K with such sources. With this
source and electron multiplier detector, species having partial pressures
as low as 10^{-12} atmospheres have been detected.

tinued, from successively deeper layers of the bulk material. On the other hand, many projectile ions penetrating the surface are "trapped", at least temporarily, in the material.

The threshold energy for sputtering is dependent both on the nature of the target material and on the mass of the bombarding ions; typically, it is 50 - 100 eV. Total sputtering yields (sputtered atoms/bombarding ion) have been found (18) to vary systematically with the position of the element in the periodic table. It has been postulated (18) that the more closely the collisions between atoms in the lattice resemble hard-sphere collisions, the higher the sputtering efficiency, and that collisions in Cu, Ag, and Au most closely resemble hard-sphere collisions.

The sputtering process produces ions as well as atoms. But it is only recently, through the use of mass spectrometers, that the sputtered ions have been studied. Mass spectrometers with ion bombardment sources have been described by several authors: Honig (19), Bradley (20), Beske (21), R. Herzog (22), Stanton (23), Smith, Marshall, Cambey and Michael (24), Kerr (25), and Liebl and R. Herzog (26).

Honig reports that for ion bombardment as well as for thermionic emission the Langmuir-Saha relations give the probability of a given particle leaving the surface as either an ion or a neutral. However, in the bombardment case, the temperature of the surface, T, may be taken to be a very high, localized temperature of the order of 30,000° K. This predicts, and it is observed, that there will be variations in ionization efficiency from element to element, but that some elements not ionized appreciably by the thermionic filament technique (3000° K max) will be ionized appreciably by ion bombardment.

Although the "temperature" in the region of bombarding particle-surface atom interactions is above 10,000° K, the quantity of heat delivered to the

specimen as a whole is very small, so that the overall temperature rise of the target can be kept well below one degree. Thus it would be possible with the ion bombardment source to study surface coatings and substances which decompose at elevated temperatures. It would also be possible to cool the target and study substances unstable at room temperature. If inert gas is used for the bombarding ion beam, the results are not complicated by chemical reactions between the bombarding ions and the target material.

Bradley (20), among others, reports wide variations in ion yield for a given element as a function of time and/or specimen temperature. This complexity of ion formation, as well as high discrimination among elements, leads one to the conclusion that study of the neutral sputtered atoms holds more promise as a chemical analysis technique than the study of the sputtered ions. For this reason the authors, among others, have used a "second" source containing an electron gun, to ionize neutrals sputtered from the target. These ions are then analyzed in the same manner as the secondary ions. A schematic diagram of a source arrangement of this type used in an instrument described by Smith et al (24) is shown in Figure 4 .

Figure 8 illustrates the kind of information that can be obtained from the analysis of sputtered ion beams. This spectrum and the spectrum shown in Figure 9 were obtained with the source arrangement shown in Figure 4 . The mass resolving system used was a 6" radius, 60° deflection magnetic analyzer. *
The sample was O. F. H. C. copper, held in an inconel holder, which in this case was also sputtered. The spectrum shows three classes of peaks: (1) ions principally formed by surface ionization (Na, K, etc.), (2) re-ionized bombarding

---

*Nuclide type DB-1

Figure 8

Spectrum of positive ions sputtered
from copper target and inconel
target holder. 6", 60° direction-
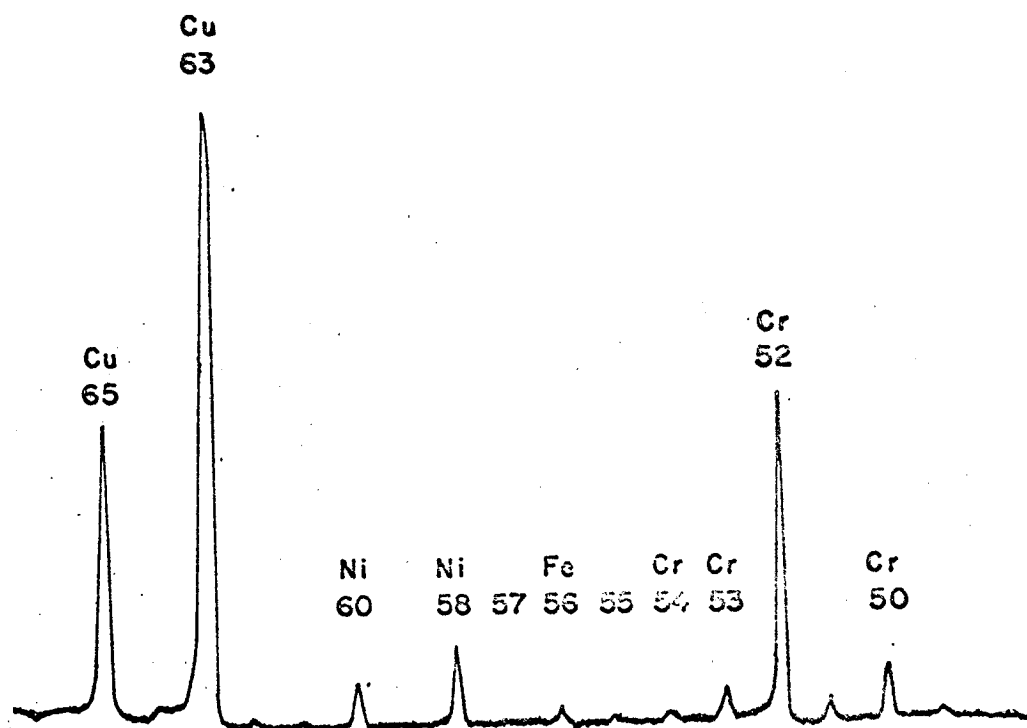focusing analyzer (Nuclide Type DB-1).
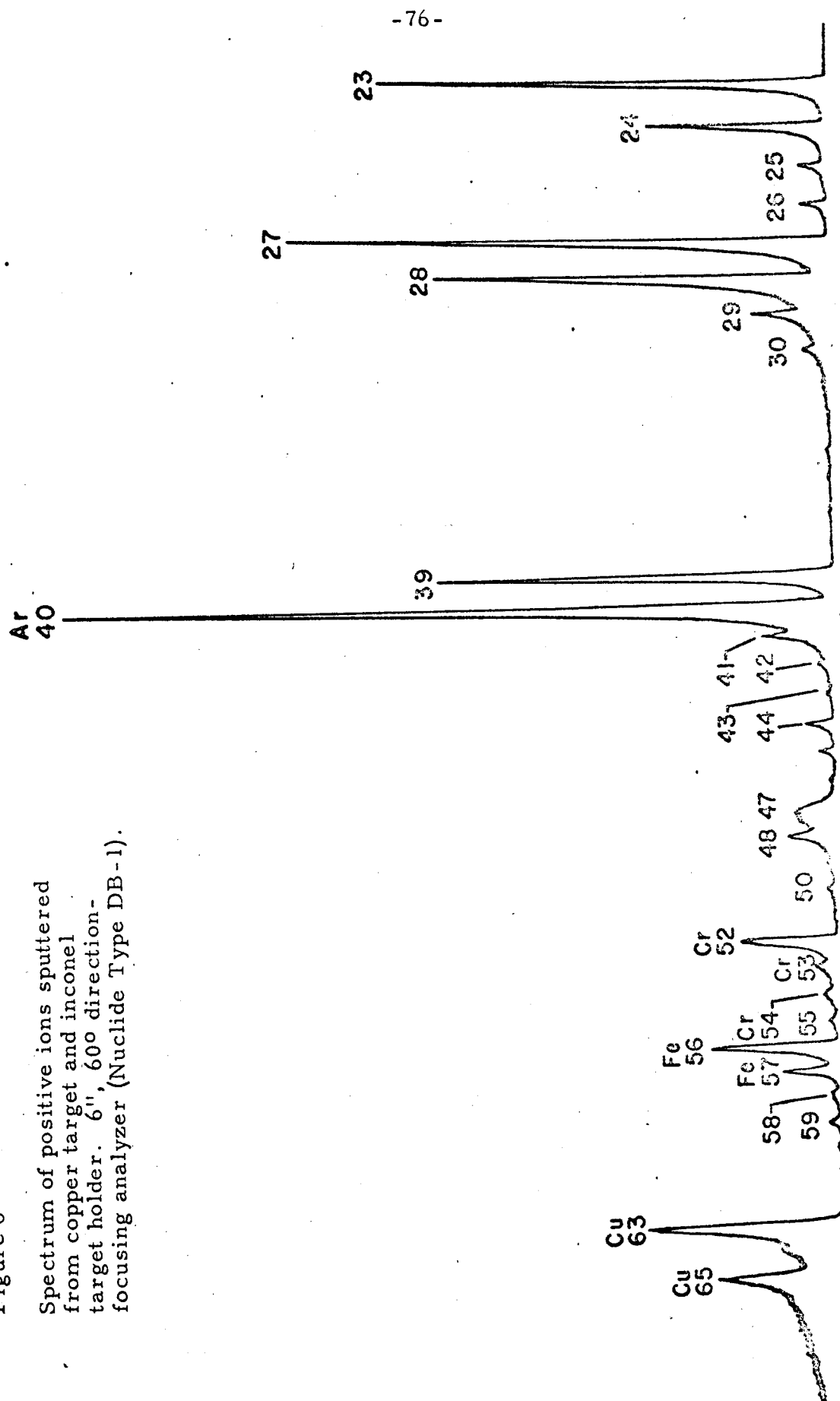
Fig. 9

Spectrum of neutral particles sputtered from Cu
target. Gas background spectrum suppressed by
use of synchronous detector system; sputtered
ion spectrum suppressed by maintaining target
at negative potential with respect to second ion
source. Same instrument used as for Figure 8.

gas (argon) ions, and (3) ions formed at least in part by a sputtering process (Cu, Fe, Cr, Ni). The sputtered ions are identified by their long high-mass "tails" and slight displacement in mass, both of which result from their distribution in energy at formation.

If the analysis is confined to the sputtered neutral atoms, a large part of the discrimination between elements is eliminated. It is not yet possible to state what fractionation remains, but it is thought to be smaller than for the ions. The neutrals may be analyzed without excessive interference from the sputtered positive ions by placing the target at a suitable negative potential with respect to the second ion source. However, as the sputtered neutrals are travelling with velocities corresponding to several electron volts, it is necessary to use high electron currents in the second source to obtain reasonable ionization efficiencies. To keep the background peaks at a tolerable level, it is also necessary either to reduce the background pressure to a very low level or to discriminate against the background peaks in some fashion so that they will not appear in the final spectrum. The severity of this problem is much greater with this type of source than with other solid sources. In an r-f spark source, it is reported that a background pressure of 10^{-6} torr of argon gives a peak equivalent in height to an impurity present in the sample of 1 ppm, whereas in this source the pressure would have to be reduced to about 10^{-14} torr to keep the background peaks down to the same relative value. In the case of a lunar analyzer, the background gas pressure would almost certainly be sufficiently low for the main sample constituents to be unobscured. Fortunately, in the sputtering source it is possible to discriminate satisfactorily against the background peaks by using a synchronous source-detector system (24, 27). Figure 9 shows an example of results obtained with this type of system.

Presently, it is not possible to state definitely the capabilities of the sputtering source for complete compositional analysis. It is felt, however, that, provided a velocity focusing (quadrupole, monopole or double-focusing magnetic) analyzer equipped with a synchronous detector is used, and only the sputtered neutrals are analyzed, this type of source may prove to be exceedingly useful for certain problems in the analysis of solids, especially for studies of surface layers.

Castaing (28) has reported on results obtained with an ion bombardment microprobe mass spectrometer system in which positive ions sputtered from the target surface are mass analyzed and focused so that a mass map of the target surface is produced. Preliminary results indicate that this technique is capable of about 10 times the spatial resolution of the well known electron microprobe X-ray analyzer technique. It also has the additional advantage that it is applicable to all elements. It has already been applied to analysis for Al, Mg, Si, Be, Cu and Ni. Depth resolution is of the order of a few millimicrons. Unfortunately, the complicated ion optical design makes it difficult to see how the equipment could be successfully miniaturized for lunar use.

3. The R-F Spark

The compositional analysis of solids by mass spectroscopy has until now been achieved principally by adaptation to this purpose of a type of instrument developed in the 1930s for the determination of atomic mass (29). In such "analytical mass spectrographs" a radio-frequency spark is used to vaporize and ionize the sample, a double-focusing ion-optical system is used for ion analysis, and a photographic plate is used to collect simultaneously and permanently record all the separated ion beams present throughout an extensive mass range, sometimes as great as mass M to 40 M.

The r-f spark source (30) utilizes two electrodes separated by a short gap. The spark is produced across the electrode gap by a pulsed r-f supply capable of delivering above 100,000 volts. The physical mechanism of the spark is not clearly understood. It has been suggested (31) that the spark is initiated by field emission. The resulting electron currents vaporize the electrodes, and the vapor is ionized by electron bombardment. The effective temperature of the spark is extremely high, 50,000° K (32). Under these conditions, differences in ionization efficiency from element to element are reduced markedly (see Table 1) in comparison to the differences encountered with some other kinds of ion sources (33) .

In addition to singly-charged ions (both positive and negative), multiply charged positive ions and ionized atom and molecule clusters are produced by such a source. Thus, since most elements have isotopes, quite a complicated mass spectrum is obtained from the r-f spark. This is a useful characteristic for mass determinations but, for chemical analysis of inorganics a simpler spectrum consisting only of singly-charged ions would, in general, be preferred.

The r-f spark source also ionizes any gases present in the source region. Thus a hydrocarbon spectrum with peaks at nearly every mass number, and several at some mass numbers, may be produced from the residual gases if the source is not very thoroughly outgassed. The problem of dealing with interferences between metal and hydrocarbon lines and between metal lines has been discussed recently by several authors (34, 35).

The energy spread of the ions leaving an r-f spark is high, $\sim$ 1000 eV (36). This makes it necessary to use a mass spectroscope equipped with an electrostatic energy "filter" to analyze the ions it produces.

As the r-f spark source operates only intermittently, the detection

system used must either integrate the collected charge, or else be able to cope with large, rapid intensity variations. A typical ion current output level with such a source is 10^{-11} amperes (average).

The results obtained with this type of source are impressive. It has been used successfully for the analysis of metals, semiconductors, insulators, liquids and powders, and part per billion (atomic) impurities have been detected in favorable cases.

4. The DC "Hot Spark" Source

Another source first tested by Dempster was the d. c. "hot spark" (37). In this source, the two electrodes are stationary. One is held at a constant potential while the potential of the other is increased as charge is fed to a condenser connected across the electrodes. When the potential becomes high enough, there is a spark breakdown. The condenser is thereby discharged, and another spark does not take place until the voltage difference has again built up to the necessary level.

The "hot spark" source seems to offer some of the same advantages for analytical work that the vibrator has, plus the advantage of being stationary. In addition, it affords an opportunity for some simplification: it is perhaps possible to use the same d. c. high voltage supply both for ion acceleration and to power the spark. At this time there is not enough information available to assess its potential for compositional analysis. However, since several groups are presently investigating this type of source, better information should be available soon.

5. Arc Sources

Operators of present r-f spark source instruments avoid long spark durations and rapid repetition rates in order to avoid overheating of electrodes

and resultant "arc-like" operation of the source. It is reported that when this occurs, large fractionation of elements results; and this is, of course, a disadvantage for routine analysis (38). However, an arc can be operated continuously, and produce copious vaporization and ionization. Further, its power supply is trivial compared to that of the r-f spark, and it does not cause electrical interference to the notorious extent of which the r-f spark is capable.

The literature of mass spectroscopy contains many descriptions of "arc" sources which produce strong ion beams; these have been used especially in isotope separators. Some of them hold promise for solids analysis also. In the "self sputtering" source developed by Druaux and Bernas (39) a discharge is initiated by gas (e.g., argon) bombardment, as in a sputtering source. The sample is inserted into the plasma and set at a negative potential of a few hundred volts. Atoms are liberated from the sample probe by sputtering and ionized by plasma and primary electrons. Ion currents of 10 - 20 mA and sample/(sample + bombarding gas) ion ratios of approximately 0.1 have been achieved for elements of the platinum group. The sputtering chamber must be at a pressure of about 10^{-3} torr in order to operate.

6. The Thermionic (Surface Ionization) Source

A major reason for the widespread use of the r-f spark source is that it is not very selective; it ionizes all elements equally well, at least within a factor of ten (40, 41). But in some studies, ion source selectivity may be an advantage.

Surface ionization is a highly selective ionization technique that dates back to Dempster's earliest work in 1918 (42). The ions produced by the "thermionic" process are singly-charged and essentially monoenergetic. Surface ionization sources can yield steady ion currents of 10^{-9} A or more, from microgram-

size samples of elements of low ionization potential, for many hours or days.

Although the total "selectivity range" of the thermionic source for all elements is well beyond 10^6*, its material-use efficiency is so good that it can be used for isotopic analysis or concentration determinations with 10^{-9} to 10^{-12} gram samples even of poorly-ionizeable elements such as uranium and plutonium. In fact, White et al report a successful analysis of 10^{-19} grams using as a detector a nuclear track plate (described below). With multiple-filament thermionic sources, it is possible to achieve analytically useful positive-ion ionization efficiencies for some 50 elements. They have the advantage of being very inefficient ionizers of hydrocarbons and of background gas.

A common thermionic source filament assembly has three filaments forming a three-sided box. The unpaired ribbon is the ionization filament and the pair at right angles to it are for sample vaporization; thus one independent control of the temperatures of vaporization and ionization. In this source the filaments are of .001" ribbon, .020" or .030" wide, fabricated of W, Ta, Pt, Re, or Mo. This "triple-filament" source was first described by Inghram and Chupka (43).

Several other configurations of vaporizers and ionizers have also proven useful, including flat single-filaments (44), single filaments on which vaporization and ionization take place at different points (45), canoe-shaped filaments (46), double filaments (47), hollow tubes (48), filaments doped with

---

*The ionization efficiency is given by the Langmuir-Saha equations, $I^+/I^o =$ exp $(e(W-I/kT)$ and $I^-/I^o =$ exp $(e(A-W/kT)$ where I^+, I^o, and I^- are respectively the predicted numbers of positive, neutral and negative particles; W is the work function of the surface (in eV), I is the first ionization potential of the element, A is the electron affinity (in eV), e is the electronic charge, k = Boltzmann's constant and T = the temperature of the emitting surface. The first ionization potentials of the elements range from 24.5 eV for He to 3.9 eV for Cs while commonly used substrates have work functions of up to about 6.5 eV.

sugar (49) or deposited platinum (50) or sintered Ta-TaO (51), as well as filaments operated in an environment of gaseous hydrocarbons (49). Continuously-oxygenated ionizing filaments have also been used and shown to greatly enhance the emitted ion intensity of some elements. Hintenberger (47), Deines and Herzog (unpublished), and Hickam and Sweeney (52) have used a thermionic source to produce both positive and negative ions. It is to be expected that in the future more and more applications in the study of solids will be developed for this simple, inexpensive and useful source.

7. Field Emission Sources

Point emitters with fields of 10^7 to 10^9 volts/cm at the tip can also be used as ion sources (53, 54). The intense electrostatic fields cause adsorbed molecules to desorb as ions. Ionization can also occur when molecules in the gas phase pass very close to the tip, but do not actually strike its surface.

Field emission ion sources have been used to ionize gases and organic vapors by Gomer and Inghram (55) and by Beckey (56, 57). The point emitter source has the useful property of giving a simple spectrum, consisting often only of the "parent" peak, when used for analyzing organic vapors. An acetone spectrum given by Gomer (58) shows a single major peak and one minor peak, compared with 18 peaks for the equivalent spectrum obtained by electron bombardment ionization. Possible applications of field emission to the analysis of non-volatile organic compounds have been suggested by Beynon (59).

There have as yet been few applications of point emitter sources to solids analysis. In one, Ionov (60) reports that field-enhanced thermionic emission made it possible to obtain useful ion production from a surface ionization source operating at temperatures as low as 50° C. At higher temperatures, a combination of field and thermionic emission would presumably allow analysis of a wide range of elements even when present in non-conducting compounds, as is expected to be the case in the lunar crust.

A major disadvantage of a single point emitter as a field emission ion source is that it yields only a small, unstable ion current. This drawback can be partially overcome by using arrays of point emitters and by employing ion optical systems which focus a large fraction of the total ion emission into the analyzer (57). Deterioration of the points and unwanted reactions with adsorbed water are additional disadvantages. Recent work (61, 62) suggests, however, that useful improvements in ion current stability and in intensity may be possible if very fine wires or sharp edges are used instead of point emitters.

The main advantages of the field emission source are simplicity, compactness, absence of hot surfaces, low power consumption, and comparatively simple mass spectra.

8. Exploding Wire

When sufficient power is supplied to a small wire from a source such as a simple condenser, the wire is quickly vaporized. The applied voltage causes an intense gas discharge, and thus a plasma is formed. Power dissipations of 10^6 to 10^8 watts with instantaneous currents of about 10^3 A are required. The total time involved is of the order of 10^{-5} seconds (63). Plumlee (64) has suggested the trial of this technique in a mass spectrometer ion source, so that its effectiveness for analyzing conducting materials could be evaluated. More important to the development of techniques for analyzing lunar materials, however, was the discovery of Leigh (65) that insulating materials could also be analyzed by coating them onto the wire surface so that they were immersed in the exploding-wire plasma.

Leigh has reported the results of experiments in which molecular beams emitted from exploding wires and from coatings on exploding wires were analyzed by a time-of-flight mass spectrometer. The ion source was pulsed in

synchronism with the application of voltage to the wire. The resulting mass spectra showed peaks corresponding to molecules from the wire, from the coatings on the wire, and from background gases.

Tests recently begun by one of the authors suggest a modified approach to the problem of solids analysis with the exploding wire. A special time-of-flight mass spectrometer and display system (66) are used, operating at a pulse repetition frequency of 100 - 200 Kc/s. The wire is first heated to several hundred degrees centigrade until most of the surface contamination is removed. The wire is then vaporized over a period of 20 - 100 microseconds, the changing composition of the molecular beam being recorded continuously. The wire is thus used as an efficient high-temperature sample heater rather then as a source of material for a plasma discharge. Present results suggest the possibility that, in this way, contributions of molecules originating from layers on the wire surface can more easily be distinguished from those emitted from the wire itself.

The exploding wire source is simple and has the advantage of accomplishing total vaporization. Its application is limited, however, because vaporization occurs in a very short time and under rapidly-changing conditions, making it necessary to use either an integrating detector (such as a photographic plate) or a very fast-scanning analyzer such as a time-of-flight mass spectrometer.

CHOICE OF AN ION SOURCE FOR A LUNAR ANALYZER

Desirable features are low power consumption, light weight, ruggedness, ability to ionize solids (and gases) without excessive element discrimination, minimum production of RF interference, and a minimum energy scatter in the ions produced.

No single type of ion source meets these specifications as well as could be desired; compromise is therefore necessary. Sources which come nearest to meeting the desired specifications are

    a) the electron bombardment ionizing type with either electron

    beam, Laser or Solar Image vaporization

    b) ion bombardment sputtering types, preferably with provision

    for ionizing neutrals

    c) the R.F. Spark

    d) Arc Source

The other types of source which have been studied can be eliminated from serious consideration at this point on the grounds of unduly short operating times (Exploding Wire), insufficient existing knowledge and difficulty of preparing and loading sample in a suitable form (Field Emission), excessive discrimination between elements (Thermionic) and lack of suitability for analysis of insulators combined with insufficient existing knowledge (DC "Hot Spark").

Advantages and disadvantages of the sources which come nearest to meeting the desired specifications are summarized in Table 5.

The conclusion of this survey is that the most desirable ion sources for the proposed lunar analyzer seem to be, in order of preference,

      1. Electron Bombardment Ionizer with Electron
      Bombardment Vaporizer

      2. Electron Bombardment Ionizer with Laser Vaporizer

      3. Ion Bombardment Sputtering Source

It is suggested that at least the first two of these, and preferably all three, be further investigated before a final commitment to any one type is made.

Source Type	Power Consumption	Weight (assuming miniaturization)	Element Discrimination	RF Interference	Ion Energy Scatter	Comments
Electron Bomb. Ionizer/Electron Bomb. Vaporizer	Medium/poor	Good	Good	Good	Good*	Latest information(67) suggests good chance of reducing power consumption
Electron Bomb. Ionizer/Laser Vaporizer	Good	Medium	Good	Good	Medium/Good*	Needs further investigation
Electron Bomb. Ionizer/Solar Image Vaporizer	Good	Poor (needs mirror and automatic drive)	Medium/Good	Good	Good*	Complex, bulky
Ion Bomb. Sputtering	Good	Medium	Medium/Good (if neutrals analyzed)	Good	Medium	Needs gas supply
RF Spark	Poor	Poor (mainly electronics)	Medium/Good	Very poor	Poor (but usable in DF instrument)	
Arc Source	Good	Medium	Not properly studied	Unknown	Medium	May need substantial gas supply

*Energy scatter is small but not negligible (energies up to a few eV)

Table 5 : Relative ratings of six ion sources for use in proposed lunar analyzer.

REFERENCES

1. Duckworth, H. W., Mass Spectroscopy (Cambridge Univ. Press, 1958), 37.

2. Giese, C., personal communication.

3. Heil, H., Zeit. Phys. 120, 212 (1942-3).

4. Finkelstein, A. T., Rev. Sci. Instrum. 11, 94 (1940).

5. Weiss, R., Rev. Sci. Instrum. 32, 397 (1961).

6. LaKomskii, V. J. et al, U.S.S.R. Patent 138767 (1961).

7. Rice, W., private communication (1963).

8. Raytheon Co., Technical Information Sheet on Lasers, "Laser Research and Application".

9. Honig, R. E., and Woolston, J. R., Applied Physics Letters 2, 138 - 140 (1963).

10. Honig, R. E., Applied Physics Letters 3, 8 (1963).

11. Lichtman, D. and Ready, J. F., Phys. Rev. Letters 10, 342 (1963).

12. Little, Arthur D., Inc., Arc Imaging Furnace, Bul. AIF-13708 (Sept. 1959).

13. Ahearn, A. J. and Hannay, N. B., Anal. Chem. 26, 1056 (1954).

14. Goldfinger, P., ASTM Committee E-14 Annual Meeting, Chicago, June 5, 1961.

15. Walker, R. F., personal communication.

16. Inghram, M. G., personal communication (1961).

17. Inghram, M. G. and Drowart, J., in High Temperature Technology (Stanford Res. Inst. and McGraw-Hill, New York) 219 (1959).

18. Wehner, G. K., and Rosenberg, D., J. Appl. Phys. 32, 887 (1961).

19. Honig, R. E., J. Appl. Phys. 29, 549 (1958).

20. Bradley, R. C., J. Appl. Phys. 30, 1 (1959); and Bradley, R. C., AFOSR-TN-58-97 Contract AF 18(600)-674 (1958).

21. Beske, H. E., Zeit. Angew. Phys. 14, 30 (1961).

22. Herzog, R. F. K., U. S. Patent 2,947,868 (Aug. 2, 1960).

23. Stanton, H. E., J. Appl. Phys. 31, 678 (1962).

24. Smith, A. J., Marshall, D. J., Cambey, L. A., and Michael, E. J., ASTM Committee E-14 Annual Meeting, San Francisco, May 1963.

25. Kerr, J. T., ASTM Committee E-14 Annual Meeting, San Francisco, May 1963.

26. Liebl, H. J., and Herzog, R. F. K., ASTM Committee E-14 Annual Meeting, San Francisco, May 1963; J. Appl. Phys. 34, 2893 (1963).

27. Smith, A. J., Cambey, L. A., and Marshall, D. J., J. Appl. Phys. 34, 2489 (1963).

28. Castaing, R. and Slodgian, G., C. R. Acad. Sci. (French) 255, No. 16, 1893-5 (Oct. 15, 1962).

29. Mattauch, J. and Herzog, R., Zeit. Phys. 89, 786 (1934).

30. Dempster, A. J., Rev. Sci. Instrum. 7, 46 (1936).

31. Meek, J. M. and Craggs, J. D., Electrical Breakdown of Gases (Clarendon Press, Oxford, 1953).

32. Akimov, E. A. and Malkov, E. P., Optics and Spectroscopy 6, 56 (1959).

33. Inghram, M. G., ASTM Special Tech. Pub. 149, (1953).

34. Robinson, C. F., Perkins, G. D., and Bell, N. W., Wright Air Development Center Tech. Report 59-107 (ASTIA Document No. 216 714), 23 (1959).

35. Brown, R., Craig, R. D., and Elliott, R. M., in Proceedings, Symposium on Mass Spectrometry, Oxford, 1961, (Pergamon Press, Oxford, in press).

36. Duckworth, H. W., Mass Spectroscopy, (Cambridge Uni. Press, 1958), 41.

37. Dempster, A. J., Rev. Sci. Instrum. 7, 46 (1936).

38. Robinson, C. F., Bell, N. W., Perkins, G. D., and Small, R. H., Wright Air Development Center Technical Report 59-107, Part III, 10 (August 1961).

39. Druaux, J. and Bernas, R., in Electromagnetically Enriched Isotopes and Mass Spectrometry (Butterworths, London, 1956) 30.

40. Craig, R. D., Errock, G. A., and Waldron, J. D., in Advances in Mass Spectrometry (Pergamon Press, London, 1959), 136.

41. Chakravarty, B., Venkatasubramanian, V. S., and Duckworth, H. E., in Proceedings, Symposium on Mass Spectrometry, Oxford, 1961 (Pergamon Press, Oxford, in press.)

42. Dempster, A. J., Phys. Rev. 11, 316 (1918).

43. Inghram, M. G. and Chupka, W. A., Rev. Sci. Instrum. 24, 518 (1953).

44. Inghram, M. G., Advances in Electronics (Academic Press) 1, 219 (1948).

45. Kendall, B. R. F., Rev. Sci. Instrum. 29, 1089 (1958).

46. Dietz, L. A., Rev. Sci. Instrum. 30, 235 (1959).

47. Hintenberger, H., Helv. Phys. Acta 24, 307 (1951).

48. Voshage, H. and Hintenberger, H., Z. Naturforsch 14a, 216 (1959).

49. Studier, Martin H., Sloth, Eric N., and Moore, Leon P., ASTM Committee E-14 Annual Meeting, Chicago, June 8, 1961.

50. Backus, M. M., Ph.D. Thesis (M.I.T., 1955).

51. Goris, Paul, ASTM Committee E-14 Annual Meeting, Chicago, June 8, 1961.

52. Hickam, W. M. and Sweeney, G., ASTM Committee E-14 Annual Meeting, Chicago, June 7, 1961.

53. Muller, E. W., Ergeb. exakt. Naturwiss. 27, 290 (1953).

54. Inghram, M. G., and Gomer, R., J. Chem. Phys. 22, 1279 (1954).

55. Gomer, R. and Inghram, M. G., J. Am. Chem. Soc. 77, 55 (1955).

56. Beckey, H. D., Z. Naturforsch. 14a, 712 (1959).

57. Beckey, H. D. and Schutte, D., Z. Instrument. 68, 302 (1960).

58. Gomer, R., Field Emission and Field Ionization (Harvard Uni. Press, Cambridge, Mass., 1961) 101.

59. Beynon, J. H., Mass Spectrometry and its Applications to Organic Chemistry, Elsevier, London, 1960) 123.

60. Ionov, N. I., Zhur. Tekh. Fiz. 26, 2200 (1956).

61. Beckey, H. D., Zeits. Instrumenten Kunde 71, 51 (1963).

62. Robertson, A. J. B., et al, Brit. J. Appl. Phys. 14, 278 (1963).

63. Bennett, F. D., Scientific American, p. 103 - 112, (May 1962).

64. Plumlee, R. H., as referred to by M. G. Inghram in Trace Analysis (John Wiley and Sons, Inc., New York) 455, (1957).

65. Leigh, C. H., ONR Tech. Rept. RAD-TR-62-19 (1962).

66. Kendall, B. R. F., Proceedings, Tenth National AVS Symposium, Boston, Mass. (1963) (in press).

67. Einstein, P. A., et al, J. Sci. Instrum. 40, 562 (1963).

Chapter 5

MASS ANALYZERS

MASS ANALYZERS

This chapter summarizes the possible techniques for mass analysis of ions in a lunar mass spectrometer. Methods of producing ion beams for injection into the analyzing region have been described in the previous chapter. Methods of detecting ions after analysis will be discussed in the succeeding chapter.

The various types of mass analyzers can be divided into the following classifications:

I. Nonmagnetic Mass Analyzers

II. Magnetic Mass Analyzers (Usable only with Monoenergetic Ion Beams)

IIIA. Mass Analyzers with Separate Electric and Magnetic Fields

IIIB. Mass Analyzers with Superimposed Electric and Magnetic Fields

IV. Mass Analyzers requiring neither Electric nor Magnetic Fields

I. Non-Magnetic Mass Analyzers

1. The Quadrupole, Monopole and Fischer Mass Filters

1A. Quadrupole

The quadrupole mass spectrometer was first described by Paul and Steinwedel (1). A more detailed paper by Paul and Raether followed (2).

The analyzer section consists of four rods positioned and interconnected as in Fig. 10. To the pairs of rods are applied potentials as follows:

$$V_x = U + V \cos wt \qquad (1)$$

$$V_y = -V_x \qquad (2)$$

where V is the amplitude of an RF sine wave and U is a superimposed DC voltage.

Theoretically, the rods should have a hyperbolic cross-section, but in practice rods with a circular cross-section can be used with good results. In such cases, R_{rod} is usually made approximately $1.16\ R_o$.
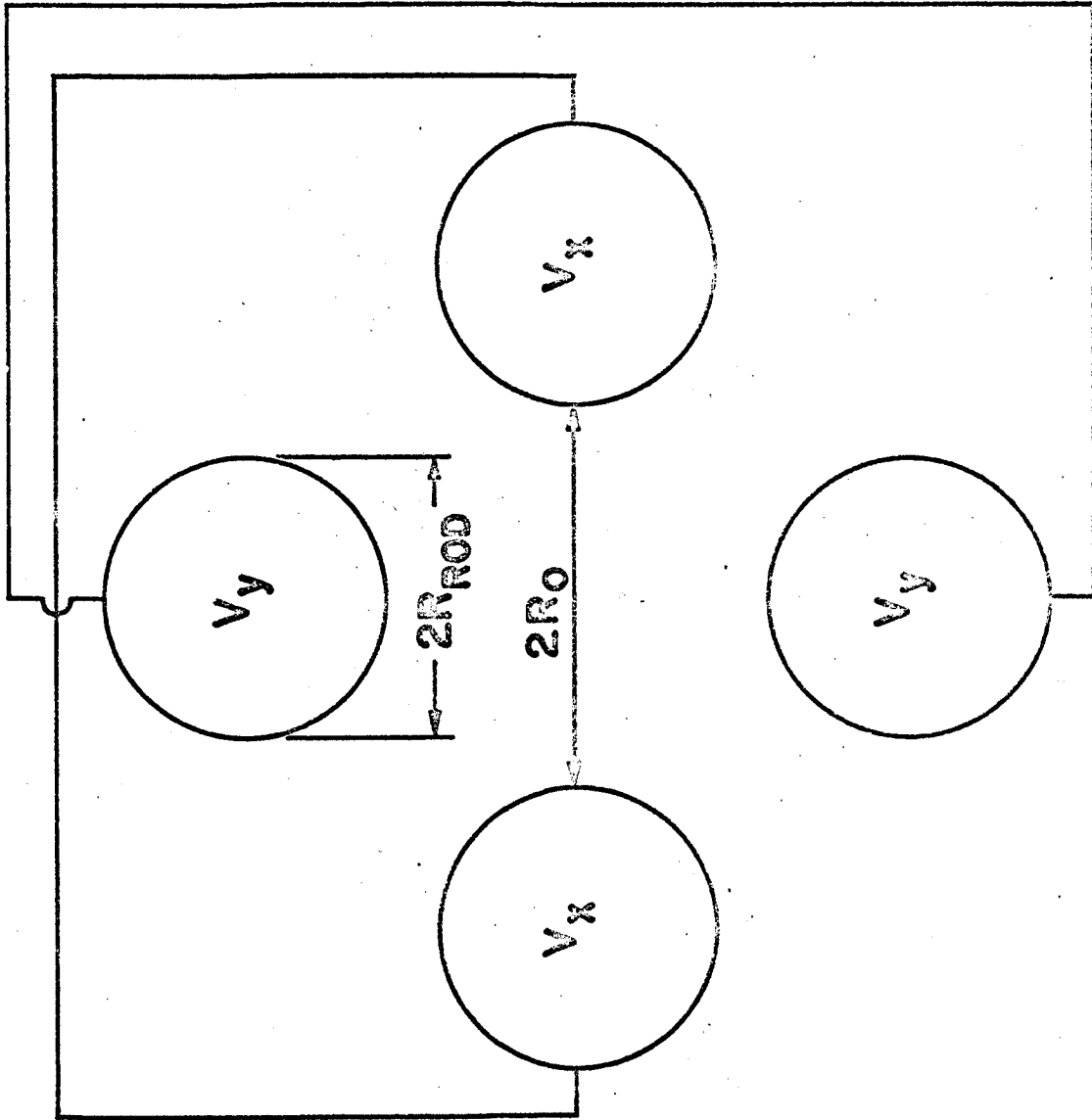
Fig. 10. Quadrupole Electrode Arrangement

When the equations of motion for an ion entering the quadrupole field are analyzed, it can be shown that ion trajectories may be either stable or unstable according to the ionic mass. This can be represented with the aid of a stability diagram (Figure 11). Along the x and y axes are plotted quantities a and q such that

$$q = K_1 \frac{V}{w^2 m} \qquad (3)$$

and

$$a = K_2 \frac{U}{w^2 m} \qquad (4)$$

where K_1 and K_2 are constants for a given quadrupole analyzer and m is the ionic mass. Singly-charged ions are assumed.

It can be seen from Fig. 2 that if the ratio $\frac{U}{V}$ is kept constant, then $\frac{a}{q}$ must be constant and can be represented as a straight line such as OY. At a suitable operating frequency, the operating point will be near O for ions with high masses; for ions with light masses the operating point will be in the region of Y. These light and heavy ions will be unstable and will not pass the analyzer. For a narrow range of masses corresponding to KL, the ions are stable and can pass through the quadrupole analyzer to a suitable detector. To tune to heavier masses, the frequency w can be decreased; to tune to lighter masses, the frequency can be increased. Alternatively, U and V can be varied together while maintaining a suitable ratio U/V. Wide-range tuning is usually carried out by a combination of these methods.

A photograph of an experimental quadrupole analyzer, with ion source attached, is shown in Fig. 12. Rod length is 25 cm. and Resolving Power approximately 50 (3).

The quadrupole has two important advantages over conventional magnetic mass analyzers:

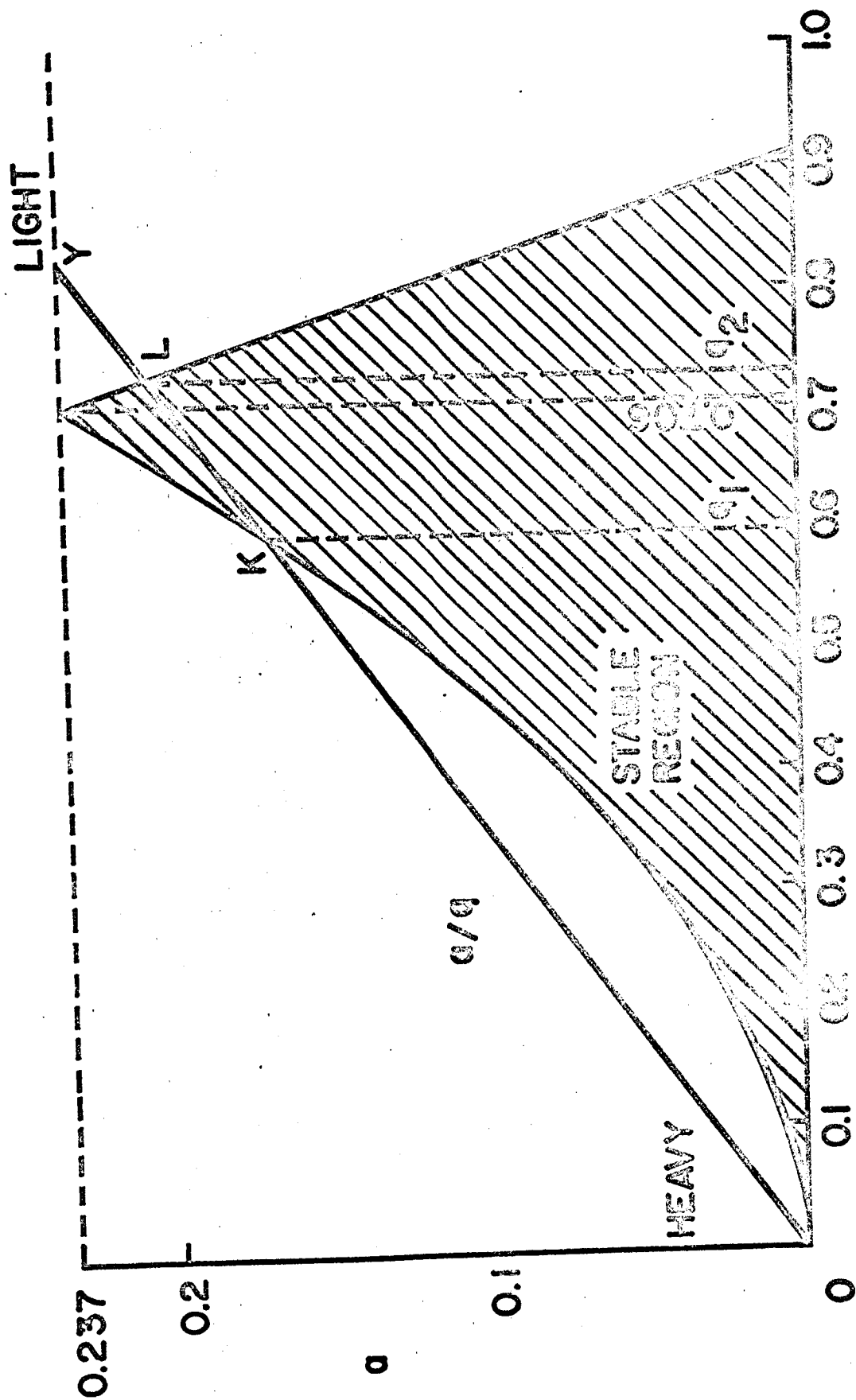   1. Initial ion energy has no direct effect on mass indications
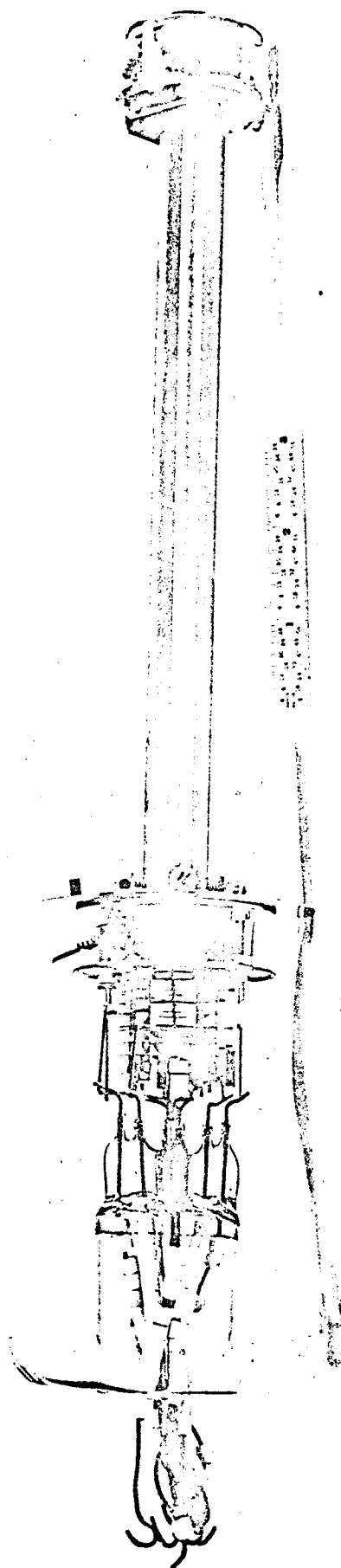
Fig. 11. Quadrupole Stability Diagram

Fig. 12. Experimental Quadrupole Mass Spectrometer

(although it may affect transmission). The analyzer is therefore velocity focusing and can be used with ion sources which give ion energy scatter.

2. There is no magnetic field.

The following disadvantages must also be considered, however:

1. Construction must be such that rod alignment is kept to quite close tolerances. There is general agreement that, with rods 10 to 25 cm. long, displacement of any one rod by more than a few thousandths of an inch may noticeably affect the performance.

2. Peaks are generally not flat-topped, which makes it more difficult to measure amplitudes accurately.

3. Simultaneous measurement of different mass peaks is not possible by any simple method.

1B. Monopole

It has been pointed out by von Zahn (4) that it is possible to produce any one of the four quadrants of the field of a quadrupole mass analyzer by means of a single rod and a right-angled grounded electrode, as in Fig. 13 . A monopole mass analyzer based on this principle has been built and successfully tested by von Zahn. The very promising results obtained suggest that the monopole deserves close attention, particularly for potential space applications.

As might be expected, the operation of a monopole mass analyzer is similar in most respects to that of a quadrupole analyzer. Mass sweeping is achieved by varying either the RF frequency or the amplitude of U and V . The monopole shares the advantages of being non-magnetic and of being insensitive to ion energy variations, and the disadvantage (common to almost all non-magnetic mass analyzers) of not normally giving a flat-topped mass peak.

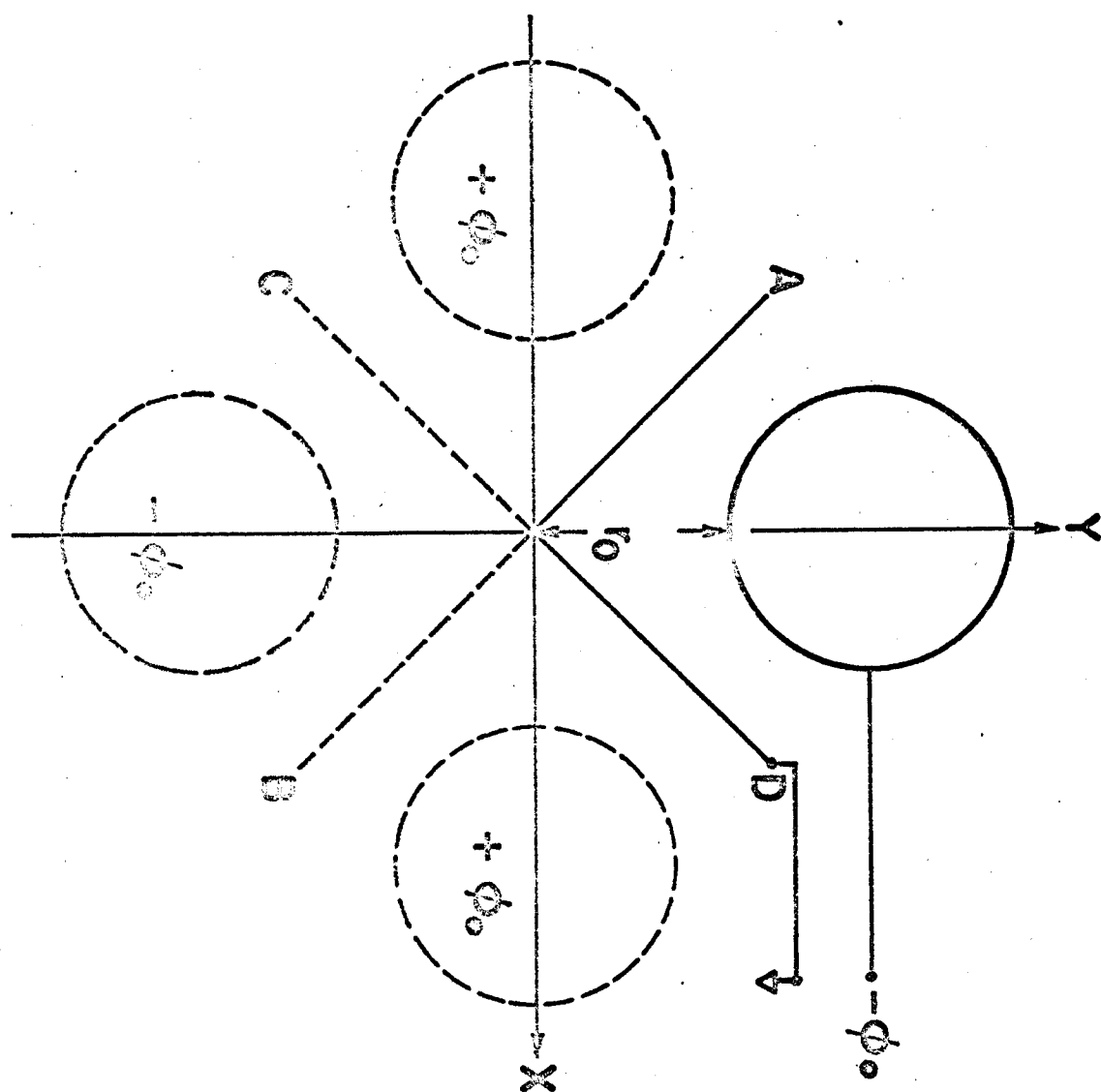The monopole has been shown by von Zahn (4) to have two very important advantages over the quadrupole:

Fig. 13. Derivation of Monopole electrode layout from Quadrupole layout.

1. The necessary stability of the ratio U/V is much reduced, so that less elaborate power supplies are needed.

2. Actual spatial separation of ions of different masses takes place, so that multiple collection is possible by means of collectors placed along the grounded electrode.

In addition, it appears that the layout is such that it would be much easier to achieve accurate positioning and rigidity of the analyzer electrodes than with a quadrupole.

An experimental and theoretical study of the monopole has recently been carried out by Redhead (5) at the National Research Council of Canada. This work has confirmed that the requirements of electrical stability for given performance are substantially reduced in the monopole as compared to the quadrupole. It appears that resolving power can be approximately doubled by changing from a quadrupole system to a monopole system of comparable size and complexity.

An example of one of von Zahn's monopole spectra showing a resolving power of 470 is given in Fig. 14.

1C. Fischer Mass Filter

This instrument appears to have been first described in the scientific literature in 1959 by Fischer, although a 1960 patent for a similar device has been assigned to Paul and Steinwedel.

The analyzer is a very compact arrangement of three electrodes, each part of a hyperboloid of revolution. Stable ions are not intercepted; they circulate continuously near the axis of the device and can be detected by measuring the inductive load presented to an external a.c. source. Unstable ions are lost by collision with the electrodes. The device can be quite sensitive. A unit of this type at CERN is said to have detected oscillating groups of only 50 electrons, and Paul (6) has detected a total of 10^4 oscillating resonant ions in a unit 5 cm. in diameter.
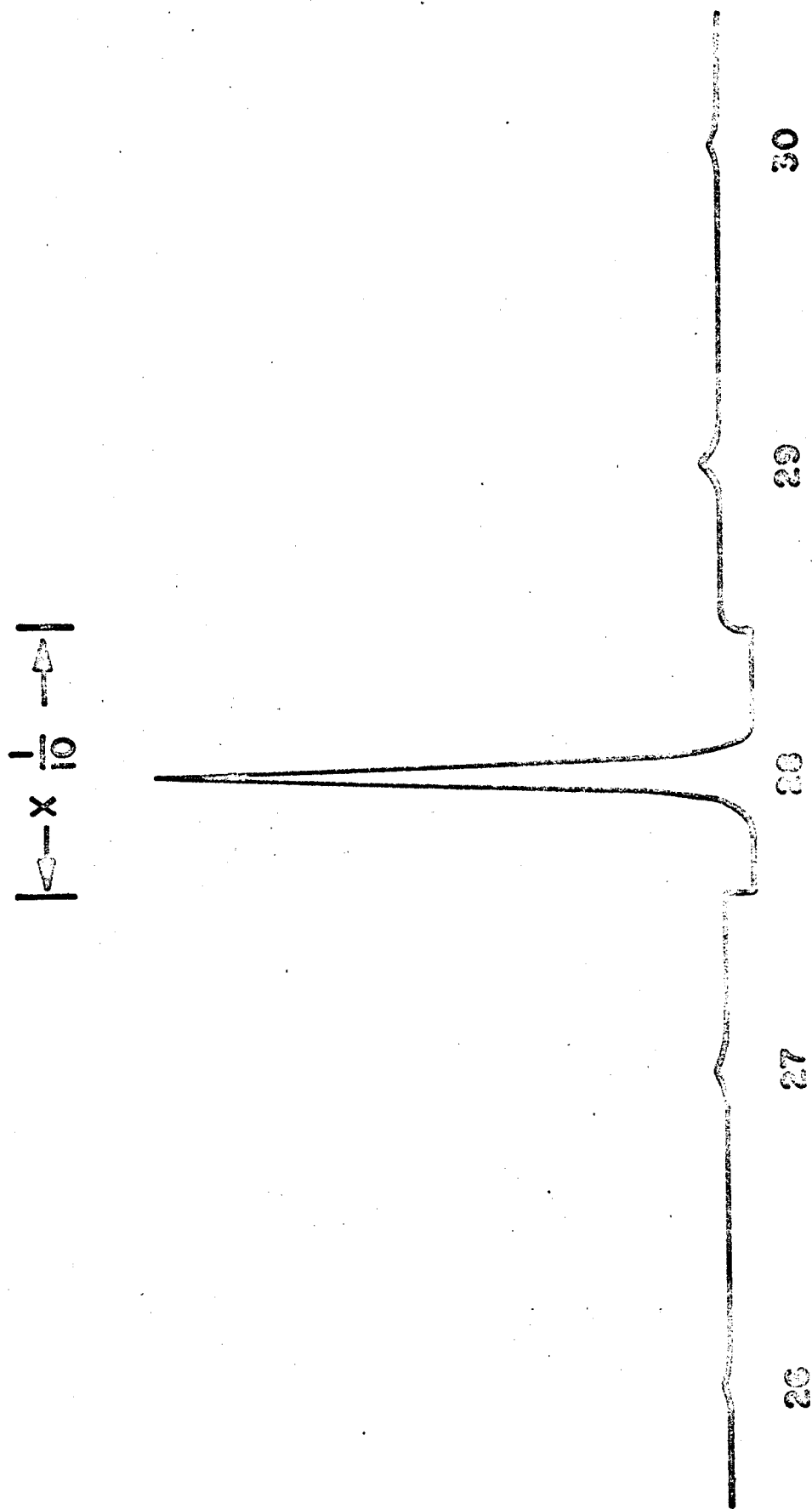
Fig. 14. Monopole spectrum showing resolving power of 470.

There is no known work being carried out in this country on the Fischer mass analyzer. Its compactness and high sensitivity suggest that further investigations would be justified.

2. Pulsed Time-of-Flight Mass Spectrometers

2A. Types with externally pulsed ion sources

In the simplest type of time-of-flight mass spectrometer, the ion source is pulsed on for very short periods (typically about 0.1μ sec) in each cycle of operation (typically lasting about 20 - 100 μsec). The ions are injected into a drift tube with identical energies. Because the time taken for an ion to traverse the drift tube is proportional to the square root of the ionic mass/charge ratio, the fluctuating signals received by a detector mounted at the end of the drift tube represent the mass spectrum of the ions emerging from the source. An instrument of this type was described by Stephens (7). An improved version, with ions injected into the drift tube with constant momentum instead of constant energy, was described by Woolf and Stephens (8).

The simple time-of-flight mass spectrometer has a very low duty ratio (typically 0.001 to 0.005, as mentioned above) and is therefore very insensitive. Much higher sensitivity was achieved by Wilson (9) who introduced an intentional energy distribution to bunch together ions of a given mass leaving the source at different times. This system gives perfect bunching for only one mass at any given time.

Interest in the time-of-flight mass spectrometer increased greatly as a result of the development of the two-field ion source by Wiley and McLaren (10). This gives the ions an intentional energy distribution to correct for the different initial positions of the ions at the beginning of the source ion extraction pulse. The duty ratio remained fairly low in the original versions of this source. More recently, however, it has been shown that ions can be stored in these sources for

relatively long periods (several microseconds) before being pulsed out into the drift tube. The effective duty ratio can be raised by this and other methods to about 0.1, and the minimum detectable partial pressure reduced accordingly to less than 10^{-12} torr (11).

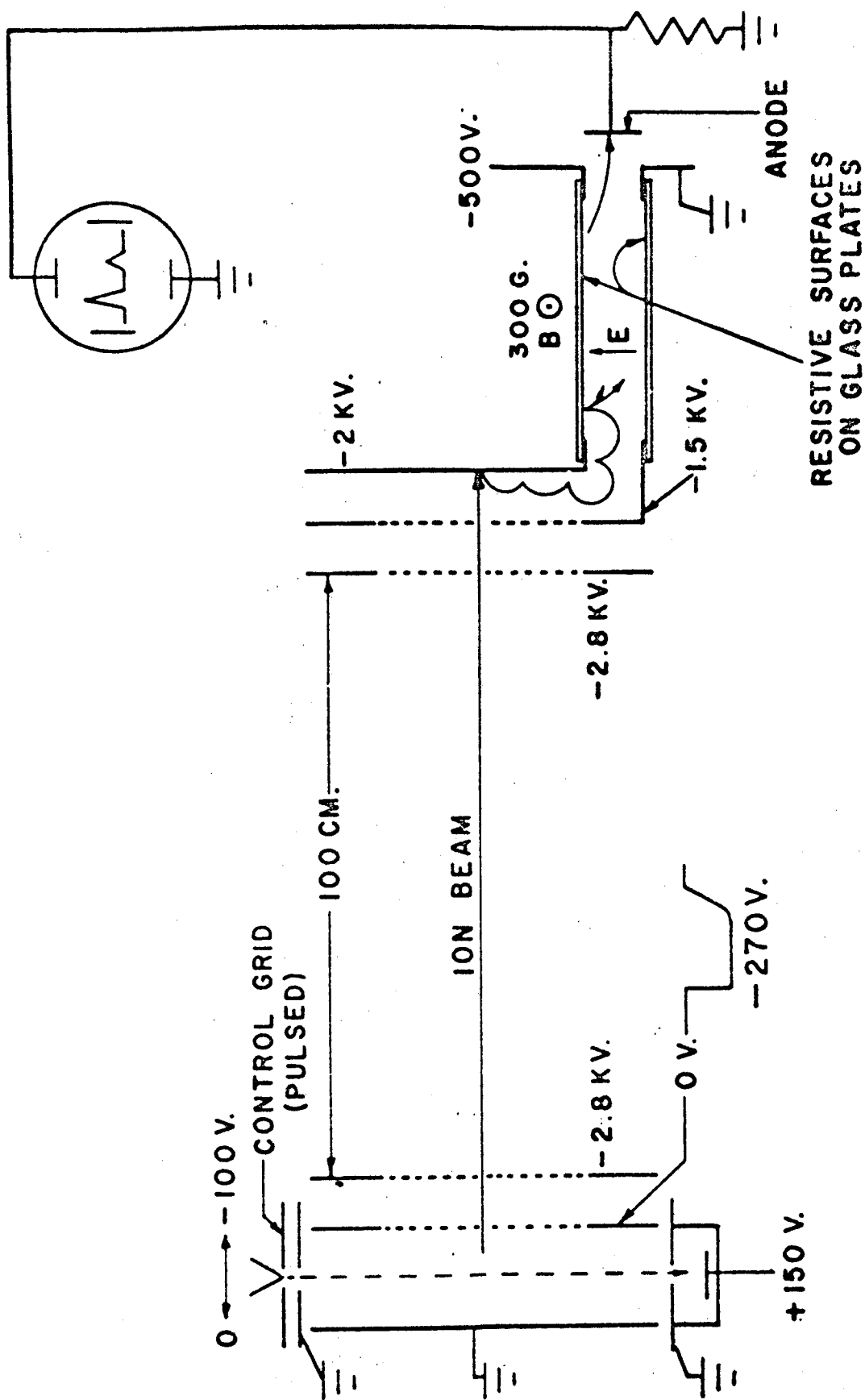A schematic of a Bendix time-of-flight mass spectrometer is shown in Fig. 15.

The layout of a small, sensitive time-of-flight mass spectrometer developed at Nuclide is shown in Figure 16. An electrostatic electron beam lens removes the need for a source magnet, and a modified venetian-blind electron multiplier removes the need for a magnetic field at the detector end. This instrument is therefore one of the few types of truly non-magnetic mass spectrometers. The drift path is at ground potential, and the ion energy is only a few hundred volts. A mass spectrum taken with this instrument at a total pressure of 7×10^{-9} torr is shown in Fig. 17.

For lunar applications the time-of-flight mass spectrometer has the advantage of being operable without magnetic fields and of being quite non-critical as to alignment. In tests, it has been shown that structural deformations which are obvious even in a casual inspection often do not completely prevent usable results from being obtained. For a given analyzer size, the time-of-flight instrument appears to give substantially inferior performance relative to a quadrupole, and even more so relative to the monopole analyzer. Kinetic energy scatter of the ions must be kept low, except for the energy variations which are intentionally introduced to achieve space-time focusing effects.

2B. The Coincidence Mass Spectrometer

A special type of time-of-flight mass spectrometer has been developed by Rosenstock (12) in which the detection system is triggered only by the detection of a secondary electron produced in the source. Because such secondaries are
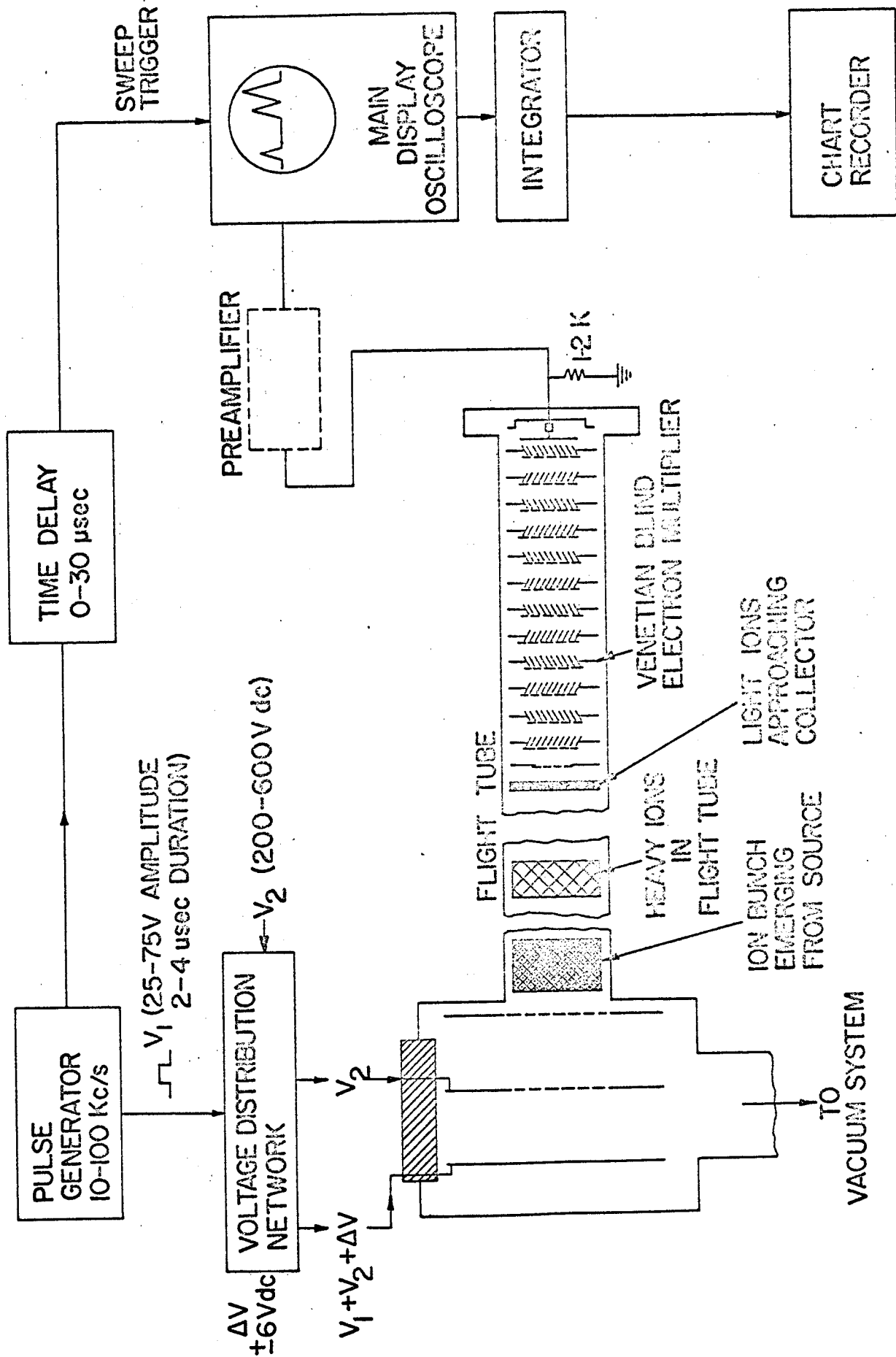
Fig. 15. Bendix-type Mass Spectrometer
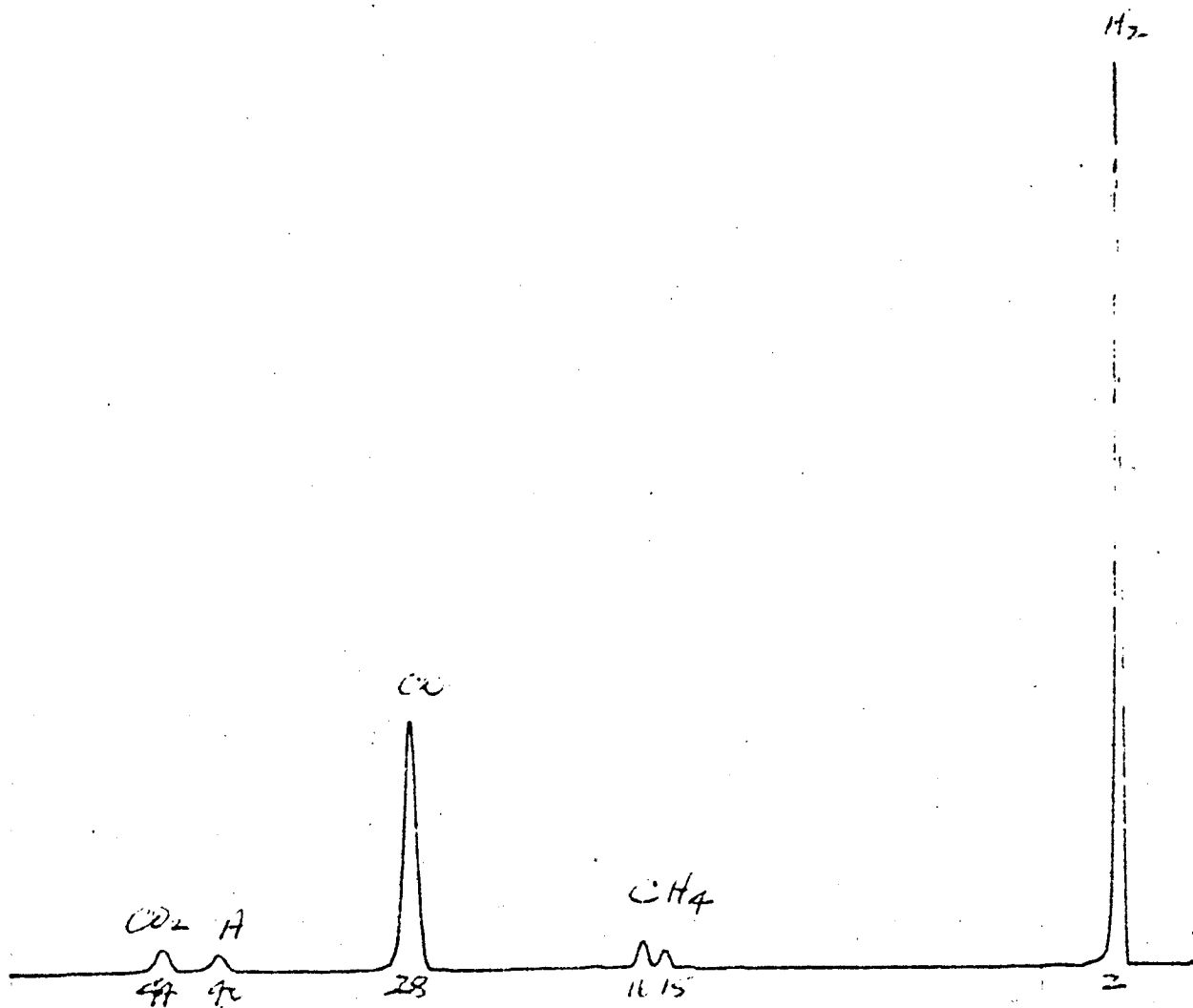
Fig. 16. Nuclide miniature TOF Mass Spectrometer

Fig. 17. Background gases at total pressure of 7 x 10^{-9} torr, as recorded by miniature time-of-flight mass spectrometer.

produced when positive ions are formed, the detector can be gated "on" only when an ion is on its way through the drift space. For extremely low sample pressures in the ion source, this affords a useful increase in detection sensitivity.

Fig. 18 shows the arrangement of a typical coincidence mass spectrometer. The primary electron beam is continuous. Secondary electrons formed during ionizing collisions between primary electrons and gas molecules trigger the oscilloscope. When the corresponding ion arrives at the detector, after a flight time dependent on the ionic mass/charge ratio, a peak is traced on the oscilloscope display. Operation is therefore similar to that of a conventional time-of-flight mass spectrometer, except that in general there is only one ion per operating cycle.

In practice both detectors are electron multipliers. The ion source is normally of the Wiley and McLaren two-field type which gives useful space/time focusing.

The simple display system shown in Fig. 18 would have two important disadvantages: –

1. If several ions were in flight at one time, only the leading ion would give a peak at the correct position on the display. The other ions would have been formed after the oscilloscope sweep had started. These would give peaks at incorrect positions on the display. This noise level could become severe at the higher ion currents.

2. Peak heights would not indicate relative partial pressures. Indicated peak height would be determined only by the gain of the multiplier, and would represent the amplitude of a single ion count rather than the frequency of ion counts.

By operating at very low total ion currents, usually in the range 500 - 1000 ions/second, the first of the two disadvantages mentioned above can be eliminated.
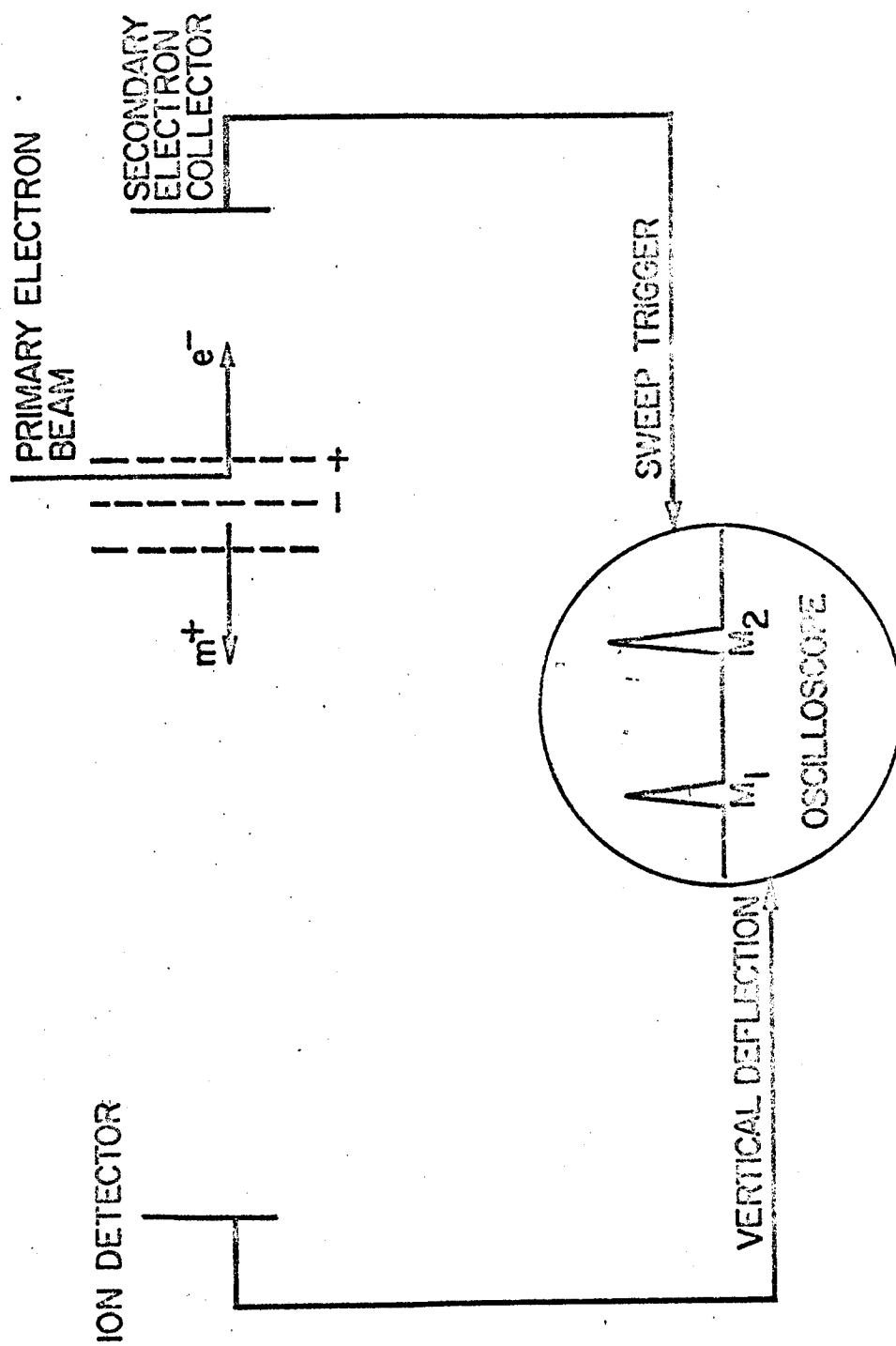
Fig. 18. Basic Coincidence Mass Spectrometer

The need for such low currents removes many of the advantages which this type of instrument would otherwise have for normal analytical work. Nevertheless, for the analysis of gases at very low total pressures (e.g., below 10^{-12} torr) where all types of analyzers necessarily operate at very low total ion currents, the coincidence mass spectrometer appears to have interesting potentialities.

In order to measure partial pressures, the number of ions collected at different masses must be averaged over a large number of operating cycles. A 10 part-per-million constituent may give rise to only 1 ion in a period of 1 to 2 minutes, so that even a semiquantitative measurement of its concentration may take up to an hour of continuous operation and information storage.

The coincidence mass spectrometer, like other time-of-flight instruments, requires that the molecules from which the ions are formed should have a fairly low energy scatter. Larger energy variations can, of course, be tolerated if suitable energy filtering is carried out either before the ions are formed or before the ion beam reaches the detector.

3. Other Non-Magnetic Mass Spectrometers

Linear radio-frequency mass spectrometers have been used widely in upper atmosphere research. The radio frequency voltages are applied to a series of electrodes spaced along a flight tube. Ions having a transit time between field regions which corresponds to the electrical phase difference between field regions are able to gain more energy than non-resonant ions. A high-pass energy filter then allows collection of only those ions which have gained a maximum of energy. Versions devised by Bennett (13) and Redhead (14) are well known. A decelerating electrode system was used by Donner (15). It is difficult to obtain resolving power exceeding about 50, and the sensitivity varies considerably with small changes in ion energy. Figure 19 shows a linear RF mass spectrometer with evenly spaced grids, developed by Redhead.
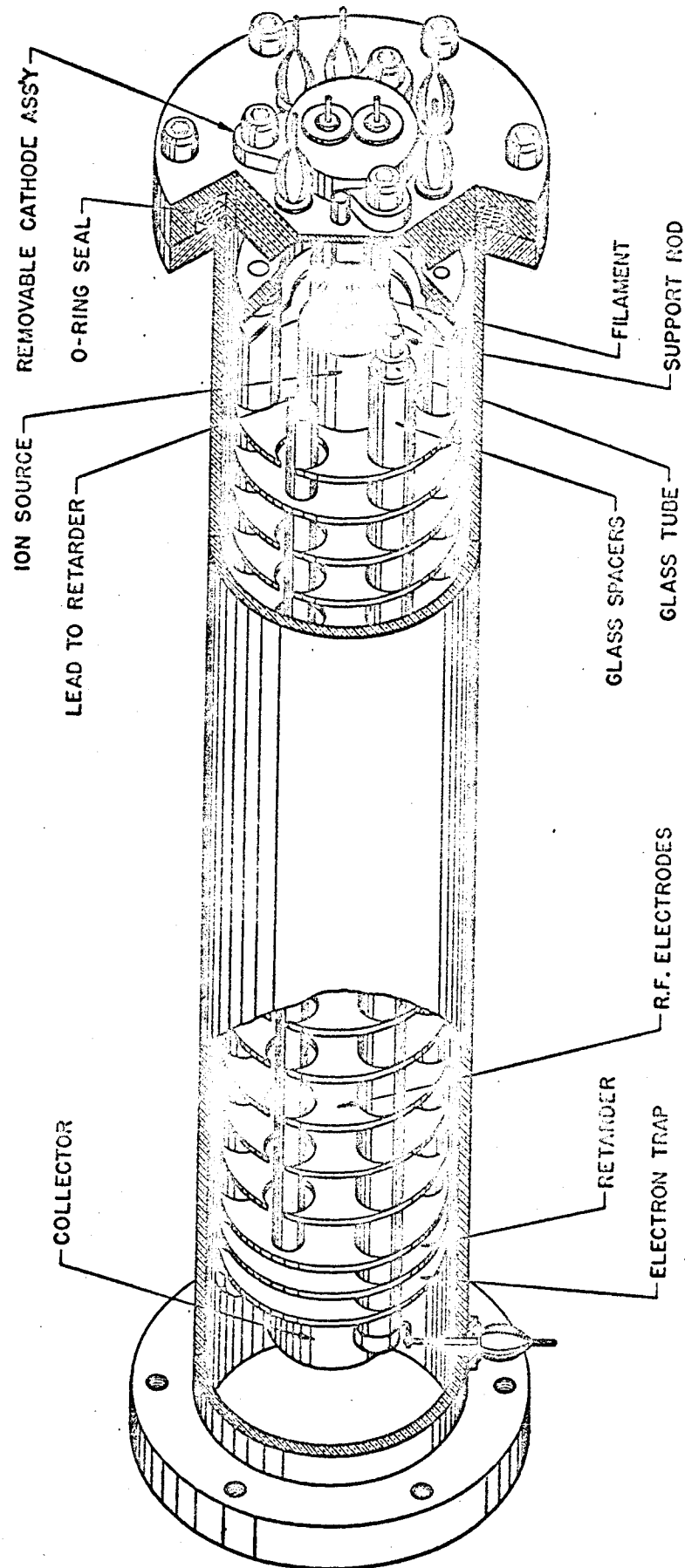
Fig. 19. Linear RF Mass Spectrometer

Linear oscillator mass spectrometers such as the Farvitron (16), Palletron (17) and ion reflecting types (18) have been demonstrated, but do not appear to offer any special advantages except perhaps where extremely small size is essential and where low resolving power can be tolerated. Similar comments apply to the constant-momentum spectrometers such as that suggested by Hipple (19) in which ion energy gain is used as an indication of ionic mass.

Rotating field mass spectrometers of various kinds have been developed. In one version, ions are injected along the axis of a tube having helical electrodes to which an RF voltage is applied. Ions having a velocity corresponding to the product of the frequency and the pitch of the helices gain maximum radial velocity. The collector is in the form of a ring. In another type (20), the ions move successively through two rotating fields with known phase difference. Flight times and phase differences between the fields determine the radial displacement of ions from the center of a circular collector. The mass spectrum is in the form of concentric rings. These instruments are mostly of low performance, with their main advantage being a comparative lack of sensitivity to small geometrical misalignments.

II. Magnetic Mass Analyzers
(Usable only with Mono-energetic Ion Beams)

Most presently envisioned lunar probe "packages" include a magnetometer for measuring the very weak lunar magnetic field. This imposes a stringent restriction on all other apparatus included in the same mission: the stray fields from such equipment must be very small. Thus magnetic mass spectrometer analyzers, which utilize strong magnets, and in fact all analyzers utilizing source magnets, magnetic electron multipliers, etc., are at a considerable disadvantage for this application because they would require elaborate magnetic shielding (except perhaps in the case of some multiple-field configurations in which the stray

fields cancel out at a distance from the analyzer). Of course, if the mass spectrometer and magnetometer are sent to the Moon on separate missions this problem does not arise and this disadvantage of magnetic mass spectrometers disappears. And this is a plan of operation that merits consideration because magnetic analyzers are presently perhaps the most highly developed class of mass spectrometers:

1. The homogeneous sector-field mass spectrometer is widely used. A 180° type with source and collector immersed in the magnetic field was described by Dempster (21). The forerunner of many present-day commercial instruments was the 60° sector-field mass spectrometer developed by Nier (22) and shown in Figure 20. A similar instrument with 90° sector angle was used by Hipple (23).
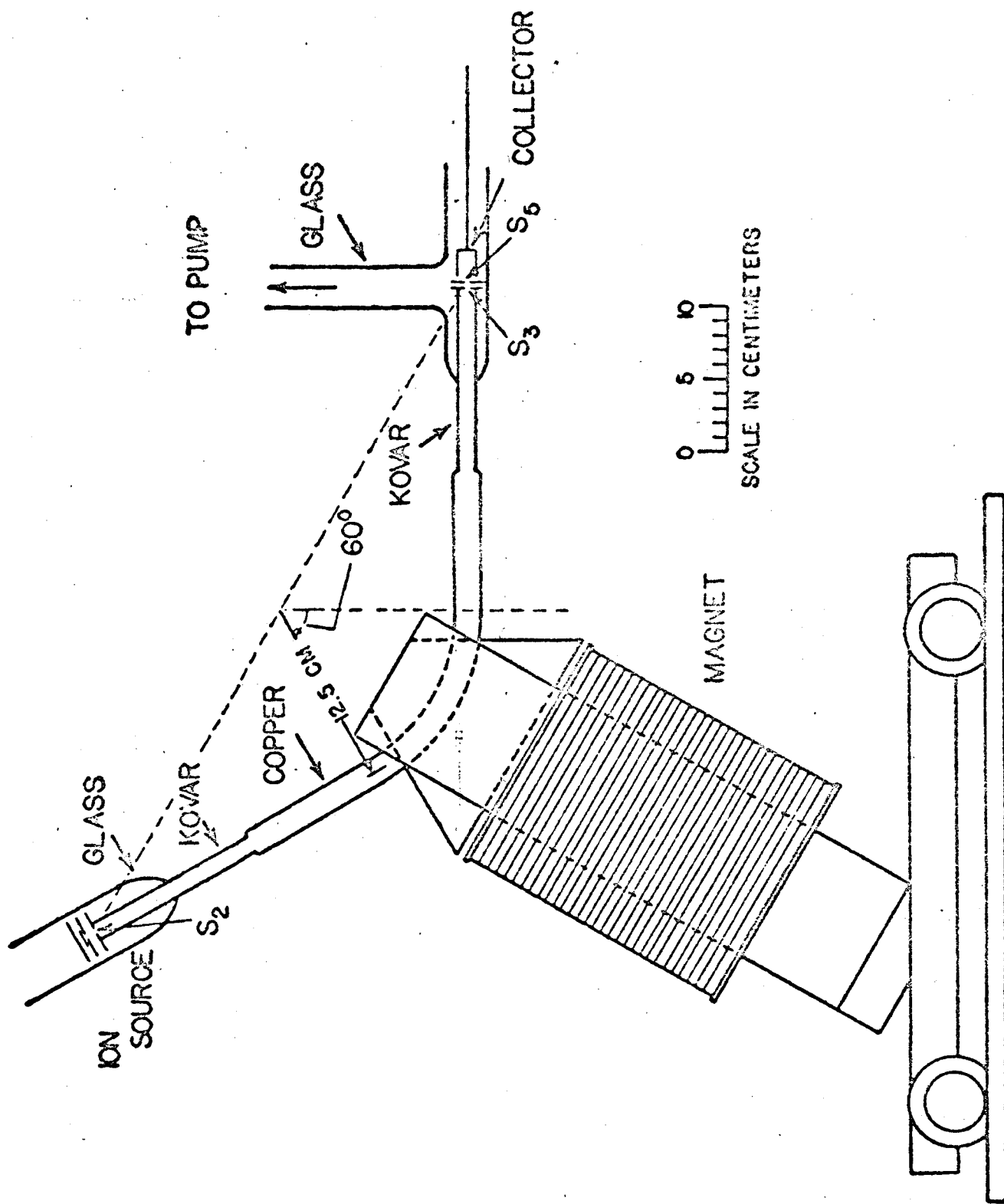
Fig. 20. Nier-type 60° sector field mass spectrometer.

Kerwin (24) has described a system with 90° sector field and 60° deflection angle which provides third-order direction focusing.

An advantage of these sector-field instruments is the large amount of effort which has been devoted to investigating their operation under various conditions. It is probably true to say that their operation is more completely understood than is the case for any other mass analyzer.

Successive sector field analyzers (25) have advantages where high abundance sensitivity is needed, and can be arranged so that the successive fields cancel out in at least two directions. Maintaining the two fields in synchronism is difficult, however, especially when permanent magnets are employed.

Very high sensitivity can be achieved with a variant in which the analyzer field is shaped so that parallel ion beams from a large planar source are focused at the collector (26).

2. Other Magnetic Analyzers

Various magnetic mass filters are known such as the circularly symmetrical filter described by Ewald (27) with a ring-shaped field and the filters described by von Ardenne (28). Although of high sensitivity because of the size of the ion source and the absence of slits, their resolving power is much inferior to that of more conventional instruments.

A helical-path analyzer described by Goudsmit (29) uses a time-of-flight principle for mass determination.

IIIA. Mass Analyzers with Separate Electric and Magnetic Fields

1. First Order Double Focus (direction and velocity)

A large number of combinations of radial electrostatic energy selectors combined with magnetic sector momentum selectors have been described. A survey of various types is given by Inghram and Hayden (30). The double focusing

feature is obviously of great importance, making it possible to use ion sources such as the RF types which give an inhomogeneous ion beam energy. The field arrangement used by Nier (31) in a flyable mass spectrometer is shown in Fig. 21..

2. Other types

A first order velocity focusing (but not direction focusing) instrument was developed by Aston (32). Crossed radial electrostatic and homogeneous circular magnetic fields were used, giving opposite deflections. This instrument is usually considered to have been the first general purpose mass spectrograph. The field arrangement is not used in modern apparatus because of the poor sensitivity and only moderate resolution, resulting from the absence of direction focusing.

In order to cope with ion beams having a large energy scatter, the Wien velocity filter (crossed superimposed electrostatic and magnetic fields) has been used on 180° and 60° magnetic sector-field momentum selectors (33, 34).

IIIB.   Mass Analyzers with Superimposed Electric and Magnetic Fields

1. Analyzers with crossed homogeneous fields

The Trochotron or cycloidal mass spectrometer (35) has crossed homogeneous electrostatic and magnetic fields. The ion trajectory is cycloidal. Normal deflection angle is 360° although multiple-orbit systems have been used. A very important advantage is the perfect direction and velocity focusing available with this configuration. A disadvantage is the difficulty of building an electron multiplier capable of operating satisfactorily in the large varying magnetic fields near the collector region, or alternatively of extracting the ion beams for detection in an external electron multiplier. Possibly a Daly-type detector would be useful in this application. Figure 22 shows a typical Trochotron layout.

If a homogeneous ion beam energy is assured, the Wien velocity filter (crossed superimposed electrostatic and magnetic fields giving equal and opposite
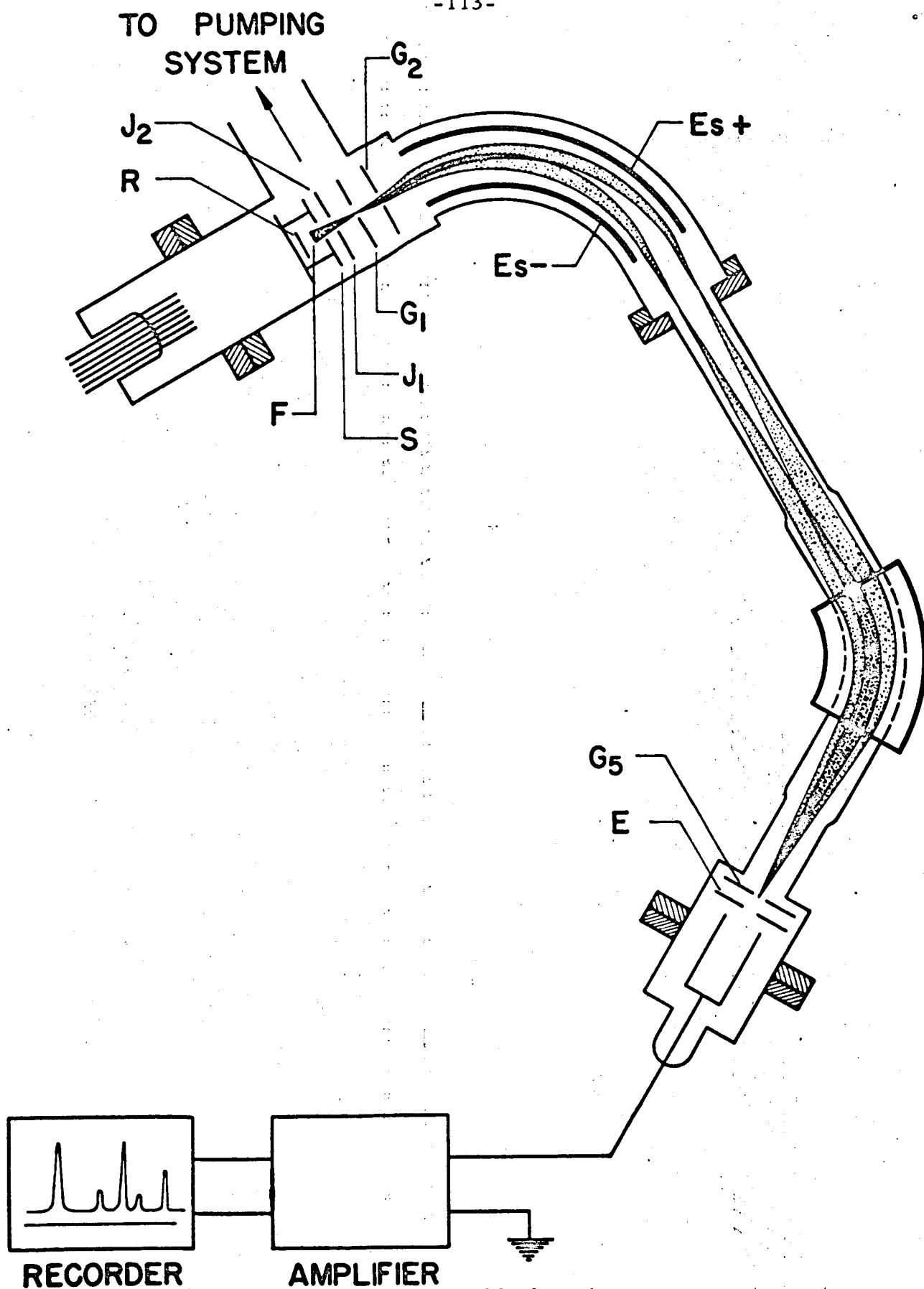
Fig. 21. Nier type flyable double focusing mass spectrometer
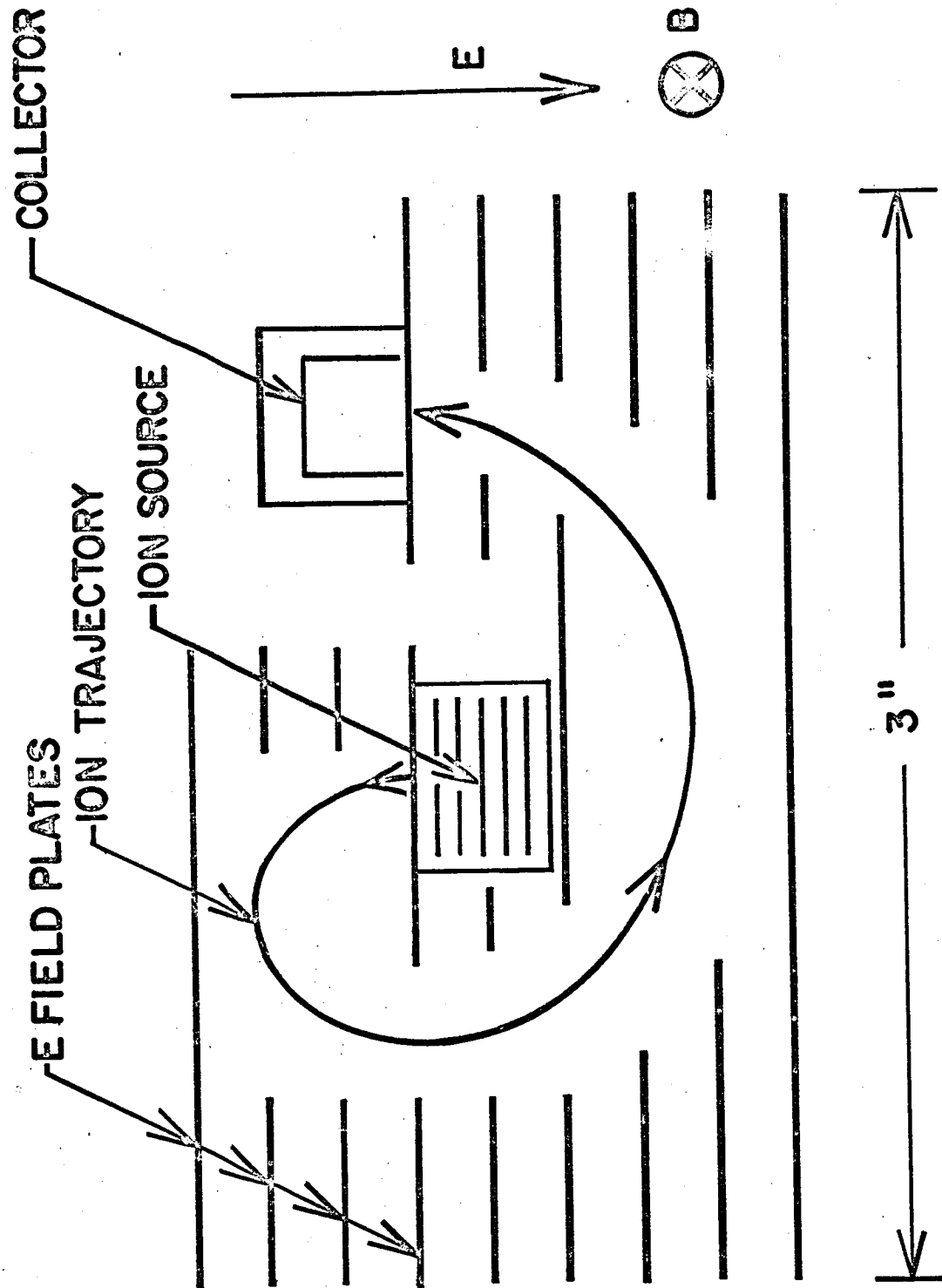
Fig. 22. Cycloidal Mass Spectrometer (Trochotron)(after Kornelsen)

deflections) can be used as a mass analyzer, passing only those ions with a pre-determined velocity. Such apparatus has been described by Bleakney (36) and by Oliphant (37).

2. Parabola Mass Spectrograph

Parallel electrostatic and magnetic fields give a parabolic image of a point source (38). Sensitivity is poor (because of the need for the point source). However, instruments of this kind are still occasionally encountered. The distributed image makes it difficult to arrange a detector system suitable for use over a wide mass range.

3. Types with crossed magnetic and alternating electrical fields

The Omegatron (39) has a central ion source and a homogeneous axial magnetic field. Resonant ions gain energy from an alternating electrical field, and increase their orbital radius until they reach a blade - like collector. Non-resonant ions remain near the axis or are extracted by a small reverse field in a direction away from the collector. A typical arrangement is shown in Fig. 23. The ionizing electron beam must be kept below about 5 μamp to avoid space-charge effects. Almost all ions formed are collected if they are resonant. As a result, the omega-tron may be characterized as a very compact mass spectrometer with low power consumption, fairly high sensitivity and the advantage of requiring no high voltage for its normal operation. It could be used for molecular-beam analysis. Unfortunately, it is almost impossible to fit an electron multiplier because the collector is immersed in the magnetic field.

Improved Omegatrons with inhomogeneous fields (40) and with a shielding-plate added to the collector region (41) have been found to give useful improvements in resolving power.

4. Other types

A first order double focusing mass spectrometer with crossed radial electro-

ELECTRON COLLECTOR

RF PLATE

RF PLATE

B

ION COLLECTOR

FILAMENT

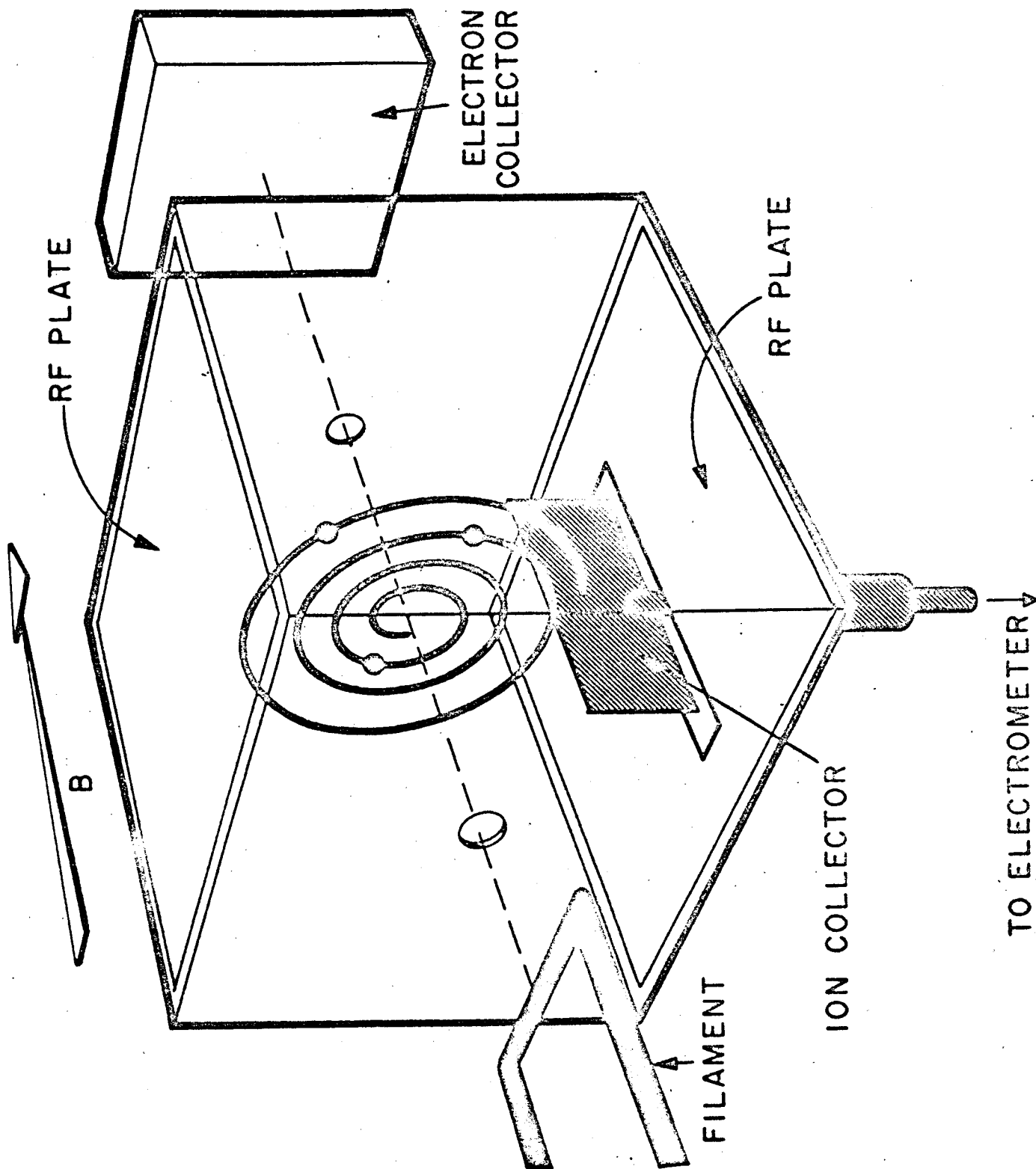TO ELECTROMETER

OMEGATRON TUBE

Fig. 23

static and homogeneous magnetic fields has been reported (42) but its advantages are not evident.

A Magnetic Lens spectrometer with the ion beam passing along the axis of a solenoid and with mass-dependent radial focusing has been described (43) but the performance was very poor at the higher masses.

Inverted magnetron mass spectrometers have been discussed by Smith (44) and by Herzog (45). Again the resolving powers were very low.

A rather complex instrument known as a mass synchrometer has been described by Smith (46). A uniform magnetic field is used. The radius of revolution of resonant ions is reduced by successive passages through a small synchronously pulsed electric field region until the ions move towards the axis sufficiently to be collected. A very high product (resolving power x sensitivity) is claimed.

IV. Mass Analyzers Requiring Neither Electric nor Magnetic Fields

One such device operates by measuring the mean wavelength of the photons emitted from a scintillation crystal during ion bombardment (47). The wavelength rises with mass number for a constant ion energy. In the first experiments, resolving power was extremely low.

Another type of detector measures both the rate of energy loss of a high-energy ion passing through a thin detector and its residual energy. From these quantities the Bethe-Bloch equation can be used to find the mass. Results showing a resolving power of about 16 for very high energy ions have been given by Anderson et al (48).

Unless a large and unexpected performance increase is obtained with these types of detectors, they must be ruled out completely for use in any lunar analyzer to be built during the next few years.

CHOICE OF A MASS ANALYZER
FOR A LUNAR MASS SPECTROMETER

General requirements are ability to operate over a wide mass range, ability to achieve a sufficiently high resolving power even when the ions emerging from the ion source have an energy range of several electron volts, minimum or zero stray magnetic field (preferably in the 0.1γ range at a distance of several feet if a magnetometer experiment is included in the mission), suitability for use with an electron multiplier detector, low power consumption, light weight, and ruggedness.

An essential feature of a suitable analyzer is the ability to detect and to measure accurately the relative abundances of O, Si, Fe, Na or K, and H_2O (as outlined in an earlier chapter); and it is highly desirable that other substances such as Al, Mg, and Ca be also measured. Detection of trace elements such as C, S, Ni, Cr and radioactive elements and decay products such as U, Th, Pb, Rb, Sr, K and Ar is also desirable. If possible, isotope ratios should be measurable for substances such as H, Li, C, O, N, Ne, Si, Fe and K. These requirements indicate a need for a mass range from mass 2 to about mass 600, and a resolving power of about 300 or higher, if feasible.

The analyzers coming nearest to meeting these requirements are

    a. Quadrupole and Monopole Mass Filters

    b. Time-of-Flight Mass Spectrometer (Pulsed)

    c. Coincidence Mass Spectrometer

    d. Sector-Field Magnetic Analyzers

    e. Double Focusing Electrostatic/Magnetic Analyzers

Other types can be eliminated on the grounds of inadequate present understanding (Fischer mass filter, scintillation and energy-loss analyzers); inadequate resolving power (the various linear RF, linear oscillator, rotating field and circular magnetic mass filters); lack of suitability for use with electron multiplier

detectors (Trochotron and Omegatron); generally inadequate performance (parabola and other early types); or complexity (the various hybrid time-of-flight/magnetic instruments).

Comparative ratings of the analyzers which come nearest to meeting the desired specifications are shown in Table 6.

The conclusion of this survey is that the most desirable types of analyzers for the proposed lunar analysis experiment seem to be, in approximate order of preference,

1. Monopole

2. Quadrupole
   Pulsed Time-of-Flight
   Coincidence

3. Double focusing Analyzer (with separate electrostatic
   and magnetic fields, as in the flyable instrument built
   by Nier).

The Monopole appears to have clear advantages because of its high performance, simplicity, lack of a magnetic field, velocity focusing, and ability to collect different ion beams simultaneously.

The three types of analyzers listed as second choice each have special features. Some of the Monopole's advantages are shared by the Quadrupole, which has been fairly thoroughly studied. The Time-of-Flight analyzers are comparatively insensitive to mechanical shock and resulting misalignment. Extreme sensitivity for analysis of very low-density gases or molecular beams is a feature of the Coincidence Mass Spectrometer.

The double focusing analyzer, preferably of the type having separate electrostatic and magnetic fields, has the disadvantage of requiring a magnet (and therefore requiring fairly elaborate shielding to obtain acceptably small stray fields if a magnetometer experiment is included in the mission). However, the performance

obtained from an instrument of given size compares well with that obtained from most non-magnetic instruments. A small flyable mass spectrometer of this type has been described by Nier (31). If future changes in mission requirements make it possible to use an analyzer which gives an appreciable stray field, this type of instrument should probably be ranked immediately below the Monopole, and might even be preferred to the Monopole if development time had to be kept to an absolute minimum.

The simple sector-field magnetic analyzer usually has a somewhat lower resolving power than a double-focusing instrument of the same size. It has the disadvantage of a further loss in resolving power when analyzing ions which may have energy variations of up to several electron volts as a result of the very high temperatures associated with electron beam or laser vaporization. Some simplification of the associated electronic equipment is possible if this type of magnetic mass spectrometer is used, because there is no electrostatic analyzer.

It is suggested that a research program to thoroughly investigate the Monopole analyzer be undertaken in the near future.

Type	Resolving Power	Ability to analyze ions with energy scatter of several e.V.	Magnetic Field Leakage	Resistance to Mech. Shock	Weight (incl. circuitry – assuming miniaturization)	Comments
Quadrupole	Good	Good	V. good (no field)	Poor/Medium	Good	
Monopole	V. good	Good	V. good (no field)	Medium	Good/V. good	Capable of simultaneous collection
Pulsed TOF	Medium	Medium*	V. good (no field)	Good	Good/V. good	
Coincidence	Medium	Medium*	V. good (no field)	Good	Medium	Max. ion current is limited to low value – but very sensitive at low pressures
Sector-Field Magnetic	Medium	Medium*	Poor/Medium (depending on shielding)	Poor/Medium	Medium	
Double-Focusing	Good	Good	Poor/Medium (depending on shielding)	Poor/Medium	Medium	

*No velocity focusing.

Table 6 : Comparative ratings of six analyzer systems for use in proposed lunar mass spectrometer.

REFERENCES

1. Paul, W. and Steinwedel, H., Z. Naturforsch 8, 448 (1953).

2. Paul, W. and Raether, M., Z. Physik 140, 262 (1955).

3. Wightman, B. A. and Redhead, P. A., Private Communications (1963).

4. von Zahn, U., Rev. Sci. Instr. 34, 1 (1963).

5. Redhead, P. A., Private Communication (1963).

6. Paul, W., Private Communication (1962).

7. Stephens, W. E., Phys. Rev. 69, 691 (1946).

8. Woolf, M. M. and Stephens, W. E., Rev. Sci. Instr. 24, 616 (1953).

9. Wilson, R. R., AECD-3373 (1952).

10. Wiley, W. C. and McLaren, I. H., Rev. Sci. Instr. 26, 1150 (1955).

11. Kendall, B. R. F., J. Sci. Instr. 39, 267 (1962).

12. Rosenstock, H. M., U. S. Patent 2,999,157.

13. Bennett, W. H., J. Appl. Phys. 21, 143 (1950).

14. Redhead, P. A., Can. J. Phys. 30, 1 (1952).

15. Donner, W., Applied Spectroscopy 8, 157 (1954).

16. Tretner, W., Z. Angew Physik 11, 395 (1959).

17. Valentini, H. B., Experimentelle Technik der Physik 8, 65 (1960).

18. Alikhanov, S. G., J. Exp. Theor. Phys. (USSR) 4, 452 (1957).

19. Hipple, J. A., 2,764,691.

20. Kramer, J. and Le Poole, J. B., Ind. Chim. Belge 19, 705 (1954).

21. Dempster, A. J., Phys. Rev. 11, 316 (1918).

22. Nier, A. O., Rev. Sci. Instr. 11, 212 (1940).

23. Hipple, J. A., J. Appl. Phys. 13, 551 (1942).

24. Kerwin, L., Rev. Sci. Instr. 21, 96 (1950).

25. Inghram, M. G. and Hess, D. C. See Inghram, M. G. and Hayden, R. J., Handbook on Mass Spectroscopy. Nuclear Science Series No. 14 (1954), pg. 17 and 23.

26. Smythe, W. R., Rumbaugh, L. H. and West, S. S., Phys. Rev. 45, 724 (1934).

27. Ewald, H. (1942). See "Methoden und Amiendungen der Massenspektroskopie" (1953) page 164.

28. von Ardenne, M., pages 471 and 472 of "Tabellen der Electronenenphysik, - Ionenphysik und Ubermikroskopie" Vol. 1 (1956 - Deutscher Verlag der Wissenschaften.).

29. Goudsmit, S. A., Phys. Rev. 74, 622 (1948).

30. Inghram, M. G. and Hayden, R. J., "Handbook on Mass Spectroscopy" (1954) page 16.

31. Nier, A. O., Rev. Sci. Instr. 31, 1127 (1960).

32. Aston, F. W., Phil. Mag. 38, 707 (1919).

33. Bainbridge, K. T., J. Franklin Inst. 215, 509 (1933).

34. Jordan, E. B., Phys. Rev. 57, 1072 (1940).

35. Bleakney, W. and Hipple, J. A., Phys. Rev. 53, 521 (1938).

36. Bleakney, W., Phys. Rev. 34, 157 (1929).

37. Oliphant, M. L. et al, Proc. Roy. Soc. A146, 922 (1934).

38. Thomson, J. J., "Rays of Positive Electricity", Longmans Green & Co. 1913.

39. Hipple, J. A. et al., Phys. Rev. 76, 1877 (1949).

40. Brubaker, W. M. and Perkins, G. D., Rev. Sci. Instr. 27, 720 (1956).

41. McNarry, L. R. and Hobson, J. P., U. S. Patent 2,958,774.

42. Bondy, H. et al., Z. Phys. 95, 46 (1935).

43. Cossutta, D. and Steckelmacher, W., Jour. Sci. Instr. 37, 404 (1960).

44. Smith, L. P. et al., Phys. Rev. 72, 989 (1947).

45. Herzog, R. F., ASTM E-14 Meeting, San Francisco, 1963.

46. Smith, L. G., Phys. Rev. 81, 295 (1951).

47. Hrehuss, G., Nuclear Instr. and Methods 8, 344 (1960).

48. Anderson, C. E. et al, Nuclear Instr. & Methods 13, 238 (1961).

Chapter 6

ION DETECTORS

ION DETECTORS

1. Faraday Cup Collector

A simple and effective electrical ion detector consists of a Faraday cup with suitable secondary electron suppressor electrodes (or magnets) and guard rings. The sensitivity of such a detector is limited by the characteristics of the current measuring device connected to it, hence a vibrating reed electrometer is often used in this application because it is capable of detecting currents as small as 2×10^{-15} A (12,000 ions/second) with a response time of about one second.

2. Electron Multipliers

The conventional electron multiplier using electrostatic focusing and separate dynodes has been widely used in mass spectrometry. In some cases multipliers of this type have been developed specifically for applications involving ion current measurement (1). Unfocused multipliers with venetian-blind and other dynode configurations are also coming into general use, particularly in cases where an ion beam having a large cross-section is to be measured. High-performance multipliers of each of these types normally have internal magnetic shielding, shielded output leads, and from 15 to 20 dynodes so that a gain of 10^6 to 10^8 can be maintained without the need for special activation procedures, which frequently give rise to undesirable fatigue effects. The unfocused multipliers have the advantage of non-critical alignment, and probably for that reason have been used rather widely in rocket-borne instrumentation.

The output pulses of an electron multiplier can either be integrated and measured with a conventional electrometer, or counted. The counting method has the advantage of being virtually independent of multiplier gain fluctuations and, when used in conjunction with pulse-height discrimination, makes it possible

to achieve background count rates as low as a few counts per hundred seconds if a properly designed multiplier is employed. Counting systems for use with mass spectrometers have been described by White and Collins (2), Cathey (3) and others. Systems are available that can accurately measure 10,000,000 cps. If a pulsed ion source such as the r-f spark source is used, the useful maximum count rate is less by the factor (time source is "on")/(total time). A 256-channel memory system for registering and storing counts at different masses has been discussed by Barton (4). Rapid progress in miniaturization of multi-channel memory systems suitable for this application suggests that it may before long be feasible to consider using this type of integrator/storage device in a lunar analyzer. In this way, results could be accumulated during long periods of running and then telemetered back to a ground station at suitable times. It would therefore be possible to operate the analyzer at quite low total ion currents while still maintaining a satisfactory overall rate of data accumulation, and without continuous use of a telemetering channel.

Multipliers with crossed electric and magnetic fields are being used increasingly. Types having separate dynodes (5) and continuous-strip dynodes (6, 7) have been developed. The continuous-strip multipliers have the advantages of simplicity of construction and small size, but frequently have a low maximum output current because of the high resistance of the dynode material. A low-noise continuous-strip multiplier in which semiconducting material is used for the dynodes, described by White et al (7), is shown in Figure 24.

Tubular multipliers with continuous dynodes have been described by Oshchepkov (8) who obtained a gain in excess of 10^4, and by Wiley and Hendee (9) who obtained a gain of 10^6. A typical layout of a tubular multiplier is shown in Figure 25. These devices have the advantage, in contrast to other resistance-
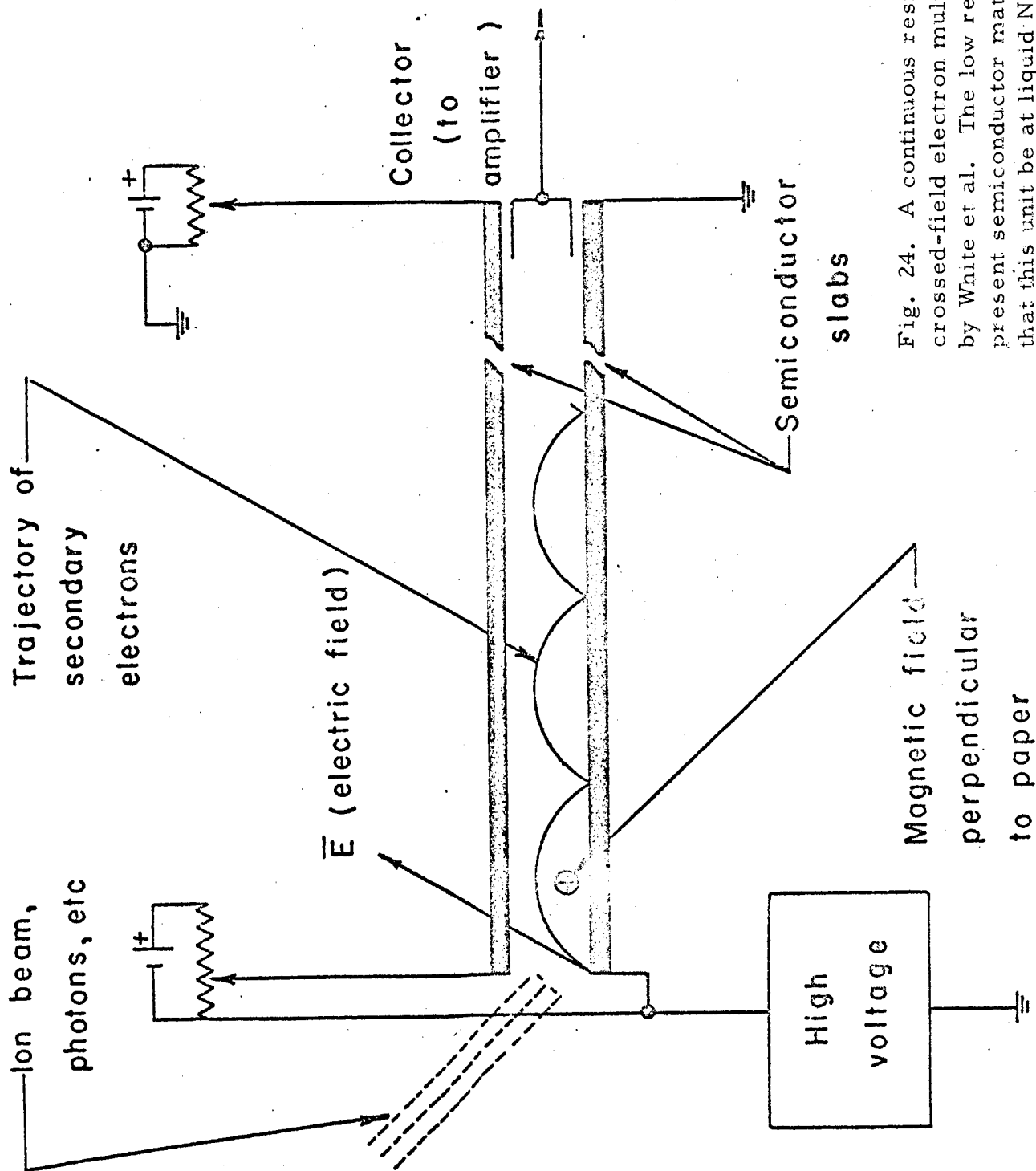
Fig. 24. A continuous resistive strip, crossed-field electron multiplier described by White et al. The low resistivity of present semiconductor materials requires that this unit be at liquid N₂ temperatures.
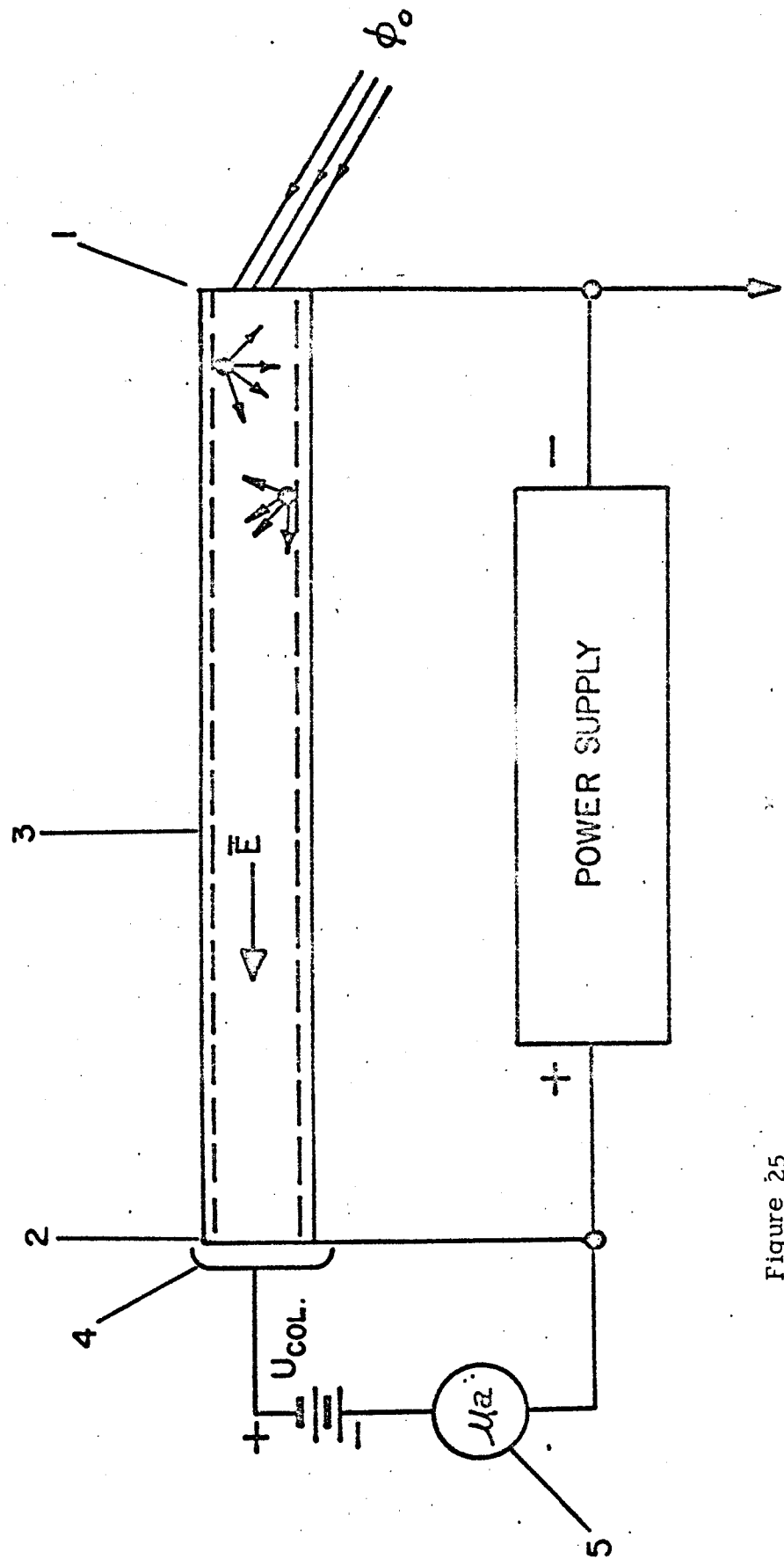
Figure 25

Tubular, continuous-strip multiplier, as used by Oshchepkov.

strip multipliers, of not requiring a magnetic field.

An increasing amount of attention is being devoted to thin-film transmission multipliers. These devices can have dynodes of sufficiently large area for many adjacent mass peaks to be registered simultaneously. Spatial relationships between the electron showers corresponding to the different peaks can be preserved by means of axial magnetic fields and large interstage voltages, so that an intensified image of part of the spectrum can be displayed on a phosphor screen or sampled at several points by means of suitable electrodes. Another method of simultaneously collecting ions at many different masses is to use stacked arrays of small multipliers. Arrays of thousands of tubular multipliers have been briefly described by Wiley and Hendee (9). Stacked arrays of continuous-dynode multipliers have been suggested by White et al (7) and others.

Figure 26 shows an experimental transmission multiplier, developed by Fenner and Wilson (10). More recently, Sternglass (11) has described a new thin film dynode which makes possible gains approaching 100 per stage with good resolution. Used in a lunar mass analyzer having a line focus for ions of different masses, a single multiplier of one of these types could be used to monitor (preferably by counting) several of the most important masses in the resolved ion beams.

3. Scintillation and Photomultiplier Detectors

One of the earliest ion detectors utilized was the fluorescent screen. A disadvantage of this detector, which was noted early, is that the positive ions cause deterioration of the fluorescent screen.

Interest in the technique revived in the late 1940s. In 1950, Richards and Hays (12) built an interesting system. The energetic ion beam was made
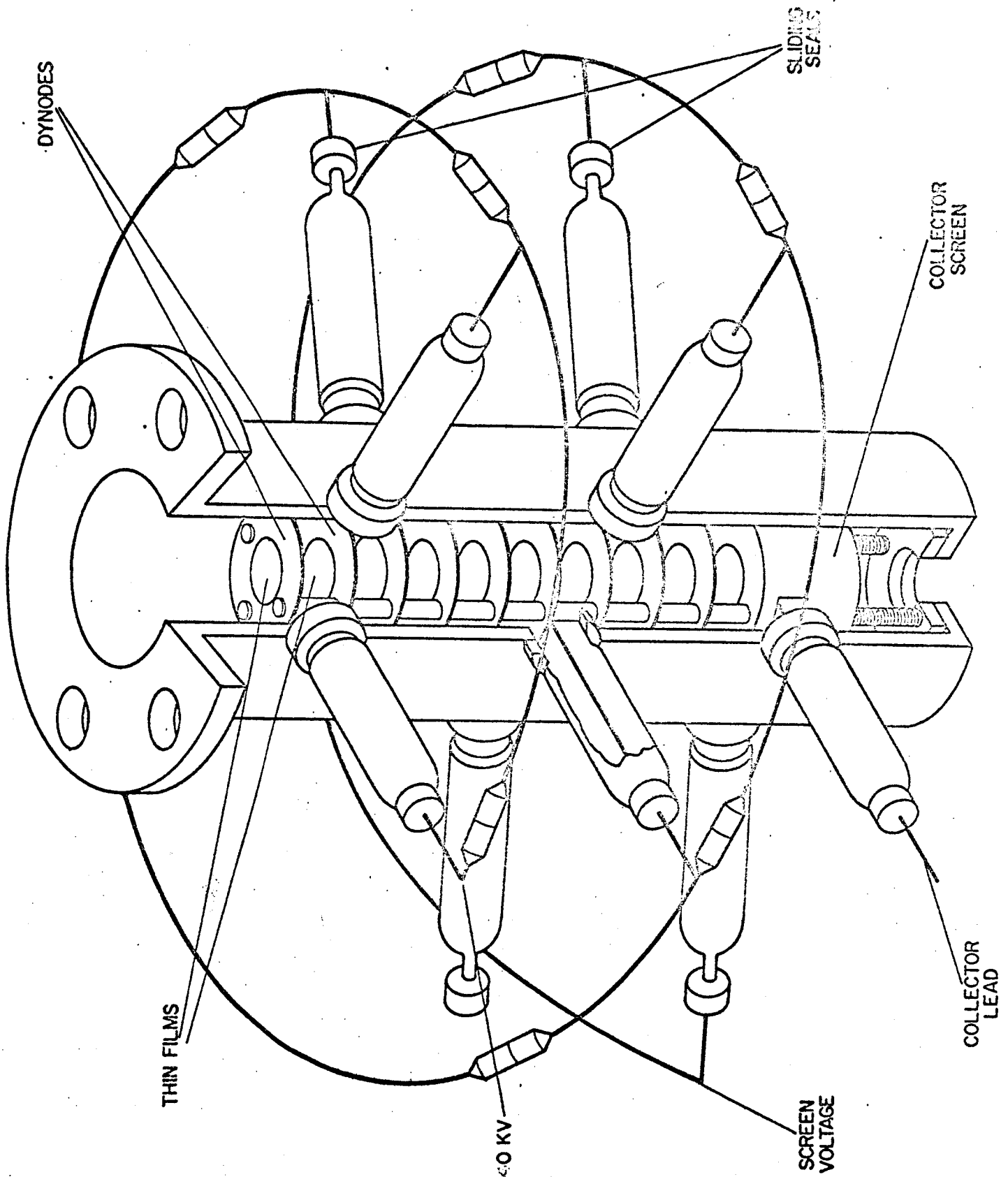
Fig. 26. Dynode arrangement in a thin-film transmission electron multiplier as described by Fenner and Wilson.

to impinge on a phosphor; the resulting photons were led out of the vacuum by a light pipe into a conventional photomultiplier tube. Ion beam damage to the phosphor was noted once again, and in addition, a strong mass discrimination effect was found. This has been confirmed by other workers (13).

A method of using a scintillation detector that avoids these difficulties has been described by Schutze and Bernhard (14), by Daly (15), and by Pikus (16). One accelerates the ions to a high total energy (say, 30 to 40 kV) and allows them to impinge on a metal electrode, often aluminum. The secondary electrons formed are accelerated onto a phosphor and the light led to the photo-multiplier. It has been reported (15) that the detector has an efficiency approaching 100% and shows no mass discrimination. However, the increased complexity relative to an electron multiplier detector and the need for a very high voltage power supply are considerable disadvantages in a lunar analyzer application.

4. The Semiconductor Detector

Friedland (17) proposed the use of a semiconductor detector consisting of a reverse-biased p-n diode. Such a diode serves as a particle detector in the following way: a distributed dipole is formed in the junction, the electron-hole pairs produced by energetic particles passing through the sensitive region are swept apart, and an electrical pulse is formed.

Presently, semiconductor detectors are used successfully in nuclear physics to detect high-energy particles, including alpha particles, protons, electrons and very energetic heavy fission fragments. By extrapolation from the results obtained, it has been estimated that light ions with energies as low as 50 keV should be detectable. As semiconductor detector technology develops, it may be expected that devices useful to mass spectrometrists will be developed.

Friedland has also suggested (17) that an array of detectors of the semi-conductor detection type might be used as an electronic analogue of a photo-graphic plate; strips with a width of 1 mm, spaced .002" apart were suggested. Certainly, there are many cases in which such an all-electronic system, detecting all masses simultaneously, would offer important advantages. However, at the time of writing, many problems remain to be worked out before a useful system can be developed. One important problem is that of poisoning. Strong ion beams deposit material rapidly, and also cause significant crystal damage. Nevertheless, it is estimated (17) that useable lives for such detectors of months or years will be achievable in normal use.

There is, however, another approach, which makes the present devices immediately useful in mass spectroscopy. As mentioned, the primary difficulty with the present semiconductor detectors is that high mass ions have difficulty in penetrating far enough into the sensitive region to produce a usable number of electron-hole pairs, unless their energy is much higher than is normally the case in mass spectroscopy. White et al (18) have overcome this difficulty by adapting a technque (described above) previously employed with scintillation detectors to convert low energy ions into energetic electrons. The ions impinge on a metal plate, and the secondary electrons produced are accelerated to the semiconductor detector. The electrons cause more effective pulse generation than the ions because of their greater range in the detector. It appears that, with an appropriate system of slits, an array of such detectors could be used for the simultaneous recording of many ion beams. However, the detection efficiency of the system described by White et al (18) was only about 10%.

SELECTION OF ION DETECTOR FOR USE IN LUNAR ANALYZER

Desirable features are light weight, low power consumption, ruggedness, ability to measure very small ion currents (down to 10^{-17} amp or preferably lower) and freedom from the need to operate at artificially reduced temperatures or in an artificially produced magnetic field.

The detectors which can reasonably be considered for use in a lunar analyzer are:

    a. Conventional Electron Multipliers of the various non-magnetic types.

    b. Tubular multiplier.

    c. Transmission-dynode multiplier.

    d. Scintillation detector.

    e. Faraday-cage collector.

Types which can be excluded from final consideration at this time include the semiconductor detector (on the grounds of insufficient development and poor performance at low ion energies) and the various multipliers which require an appreciable magnetic field for satisfactory operation and have no corresponding special advantages.

Relative ratings of the more suitable types of ion detectors are shown in Table 7.

After taking into account the advantages and disadvantages of these detector systems the conclusion of this study is that, for use in a lunar analyzer, the most suitable types of detectors in order of preference are:

    1. Conventional-type Electron Multiplier (preferably with unfocused dynodes).

    2. Tubular Electron Multiplier (Non-magnetic).

If simultaneous collection of different ion beams is desired, a multiplicity of these units could be used, operated from the same power supply. For use on a time-of-flight mass spectrometer, where the ion-electron conversion dynode must be flat or nearly so, a modified venetian-blind configuration or a Weiss-type mesh dynode could be used at the multiplier input.

Type	Weight	Power Consumption (incl. amplifier)	Ruggedness	Sensitivity	Comments
Electron Multiplier (Conventional, separate dynodes)	Good	Good	Focused - Medium Unfocused - Good	Focused - Very good. Unfocused - good.	Unfocused (e.g., venetian-blind type) dynodes may be preferable in lunar analyzer because alignment is less critical.
Tubular E. M.	Good	Good	V. Good	Good (but see comment)	Output may be limited by film resistance. Gain somewhat lower than conventional types. Could be very rugged.
Transmission-Dynode E. M.	Medium	Medium	Poor to Medium, depending on dynode construction	V. Good	Suitable for detecting many masses simultaneously. Not yet thoroughly investigated.
Scintillation-Photomultiplier Detector	Medium/Good	Medium	Medium/Good	V. Good	Sealed Multiplier feature is not significant in lunar application.
Faraday Cage	V. Good	V. Good	V. Good	Poor	

Table 7 : Comparative Ratings of Ion Detectors for Use in Lunar Analyzer

1. Marshall, D. J. and Herzog, L. F., ASTM Committee E-14 Annual Meeting, Atlantic City, (1960); also, Nuclide Corporation Technical Bulletin EM-1.

2. White, F. A. and Collins, T. L., Applied Spectroscopy 8, 17 (1954).

3. Cathey, LeC., OTS Rept. AT(07-2)-1 (August 1960).

4. Barton, G. W., Gibson, L. E., and Tolman, L. F., Anal. Chem. 32, 1599 (1960).

5. Smith, L. G., Rev. Sci. Instrum. 22, 166 (1951).

6. Goodrich, G. W., and Wiley, W. C., Rev. Sci. Instrum. 32, 846 (1961).

7. White, F. A., Sheffield, J. C., and Davis, W. D., Nucleonics 19, 58 (1961).

8. Oshchepkov, P. K. et al, Instrum. and Exper. Tech. 4, 611 (1960).

9. Wiley, W. C. and Hendee, C. F., Eighth Scintillation Counter and Semi-conductor Detector Symposium, Washington (1962).

10. Fenner, N. C. and Wilson, H. W., AWRE Report NR/P-6/61 (United Kingdom Atomic Energy Authority) (1961).

11. Sternglass, E. J., Eighth Scintillation Counter and Semiconductor Detector Symposium, Washington (1962).

12. Richard, P. I. and Hays, E. E., Rev. Sci. Instrum. 21, 99 (1950).

13. Eve, C. F. and Duckworth, H. E., Can. J. Phys. 36, 104 (1958).

14. Schutze, W. and Bernard, F., Zeit. Physik. 145, 44 (1956).

15. Daly, N. R., Rev. Sci. Instrum. 31, 720 (1960).

16. Pikus, G. Ya., Instrum. and Exper. Tech. No. 2, 286 (March - April 1960).

17. Friedland, Stephen S., ASTM Committee E-14 Annual Meeting, Chicago, June 7, 1961.

18. White, F. A., Rourke, F. M., Sheffield, J. C. and Dietz, L. A., IRE Transactions on Nuclear Science, NS-8, No. 2, 13-21 (April 1961).

Chapter 7

DATA PROCESSING AND CALIBRATION

DATA PROCESSING AND CALIBRATION

INTRODUCTION

The extremely high cost of carrying out the proposed lunar analysis makes it essential that the maximum of information be extracted from the mass spectra telemetered back to Earth after a successful landing. Consideration must also be given to the problem of obtaining information from spectra which are distorted as a result of a hard landing causing misalignment or minor structural damage to the analyzer. As an aid to the interpretation of results, calibration samples of known composition should be analyzed at intervals.

1. Spectrum Averaging

An improved signal-to-noise ratio can be obtained by integrating signals occurring at corresponding points in successive mass sweeps. Because true signals add arithmetically while noise adds randomly, the signal-to-noise ratio is improved by a factor equal to the square root of the number of integrated (i. e., averaged) spectra.

Presently available methods for spectrum averaging include use of 400-channel digital magnetic-core memories and a variety of less accurate techniques based on analog magnetic tape memories.

It is interesting to note that the inherently fast-scanning pulsed time-of-flight and coincidence mass spectrometers require an internal gating and integrating circuit in order to obtain signals suitable for telemetering.

2. Resolving-Power Multiplier

This device (1, 2) provides a means of increasing the effective resolving power of mass spectrometers (and some other kinds of spectrometers as well). It is based on the fact that signals generated by a self-adjusting analog mass spectrometer, automatically made to duplicate the output spectrum of a real mass spectrometer, can be used as an indication of the input to the real mass spectrometer. These signals

can be displayed in the form of a spectrum having a resolution considerably better than that of the real mass spectrometer alone.

The resolving-power multiplier is capable of operating satisfactorily even when there is gross overlapping of the peaks in the mass spectrum provided by the real mass spectrometer. It has the additional advantage of correcting automatically for any instrument aberration which is simulated by an exactly similar aberration built into the analog spectrometer. It could thus be used to correct for misalignment or other damage to the lunar mass spectrometer provided suitable calibration substances of known composition could be run and the distorted spectra telemetered accurately.

The practicality of the resolving-power multiplication technique depends largely on the complexity of the analog mass spectrometer required in any particular case. Fortunately, a mass spectrometer can readily be simulated in analog form when the following conditions are met:—

1. Peaks having approximately the same mass number must have the same characteristic shapes when their amplitudes are normalized.

2. It must be possible to record and store these characteristic peak shapes for each mass range to be studied.

3. The characteristic peak shapes must be stable throughout an experiment.

4. Peaks must add linearly when they overlap.

5. The mass range to be studied must be bounded by points at which there is small or zero ion current.

Experiments carried out so far have been conducted with simplified apparatus which makes it necessary for two additional requirements to be met:

6. Peaks corresponding to other than integral mass numbers will not be encountered.

7. The mass scale must be accurately calibrated.

These last requirements would be unnecessary if a more elaborate analog system were used.

a. Principle of Operation

A block diagram illustrating the basic principle of the resolving-power multiplier is shown in Fig. 27. Feedback paths are provided in such a way that the output spectrum of the analog mass spectrometer tends, by successive approximations, to become identical with the output spectrum of the real mass spectrometer. When these output spectra are identical, the internally generated signals appearing at the input of the analog mass spectrometer correspond to the input to the analyzer of the real mass spectrometer. These internally generated signals can therefore be used to identify the ionic species present at the input of the mass analyzer, and to indicate their relative abundances. This information can be displayed in the form of a spectrum in which the component peaks are completely resolved.

In practice, the performance of such a system is limited by the ability of the analog instrument to simulate the exact behavior of the real instrument, and by the ability of the feedback circuitry to provide convergence to a stable solution, as well as by the accuracy of the information supplied to the system from the real instrument. It therefore becomes necessary to make compromises between over-all performance and such factors as circuit complexity and component tolerances. Useful performance is nevertheless obtainable from systems of comparatively simple design.

Figure 28 shows a simplified schematic diagram of an early experimental resolving-power multiplier. Information from the real mass spectrometer is applied to the terminals A_1, A_2, A_3, $\cdots$, in the form of voltages between these
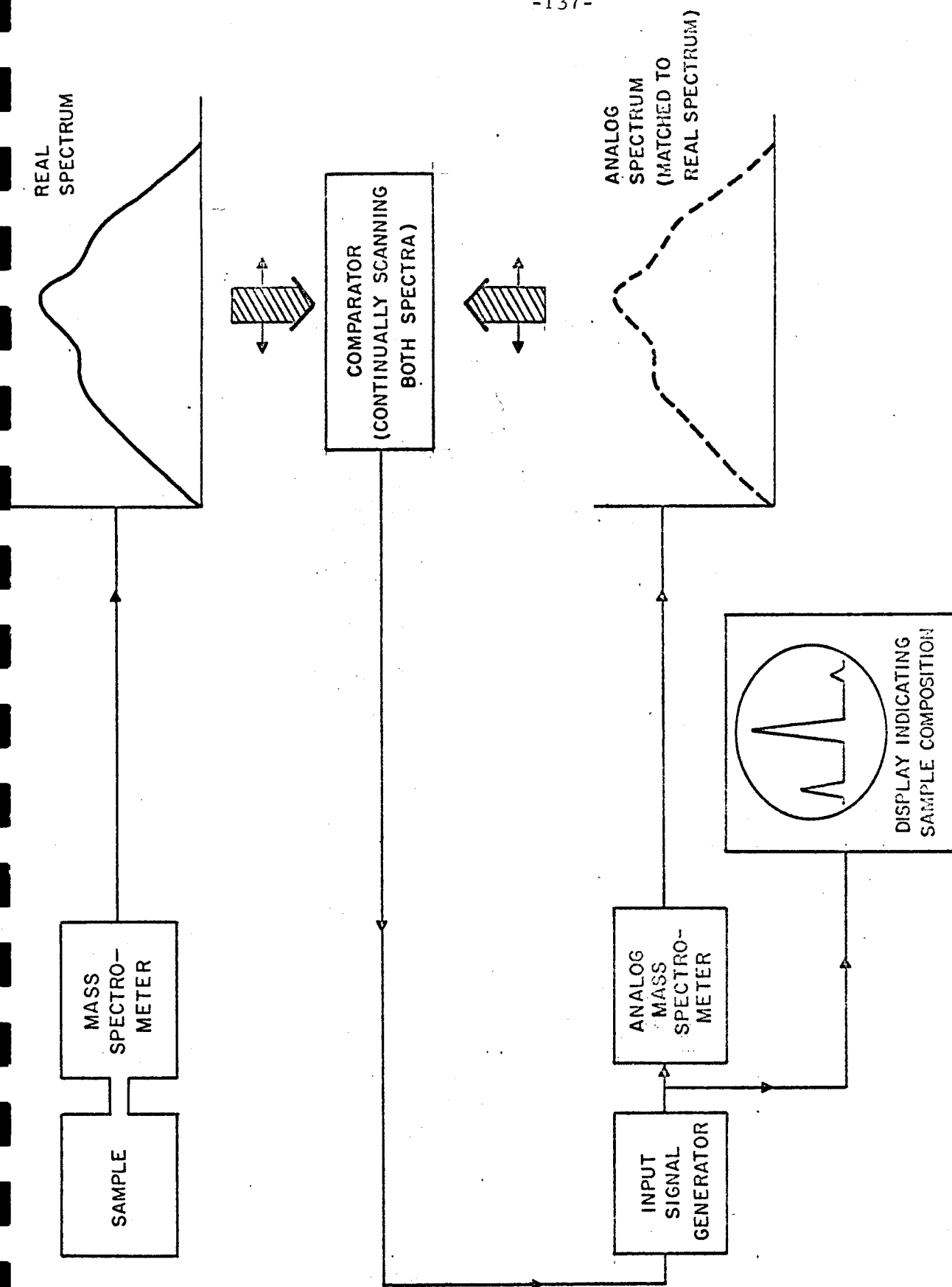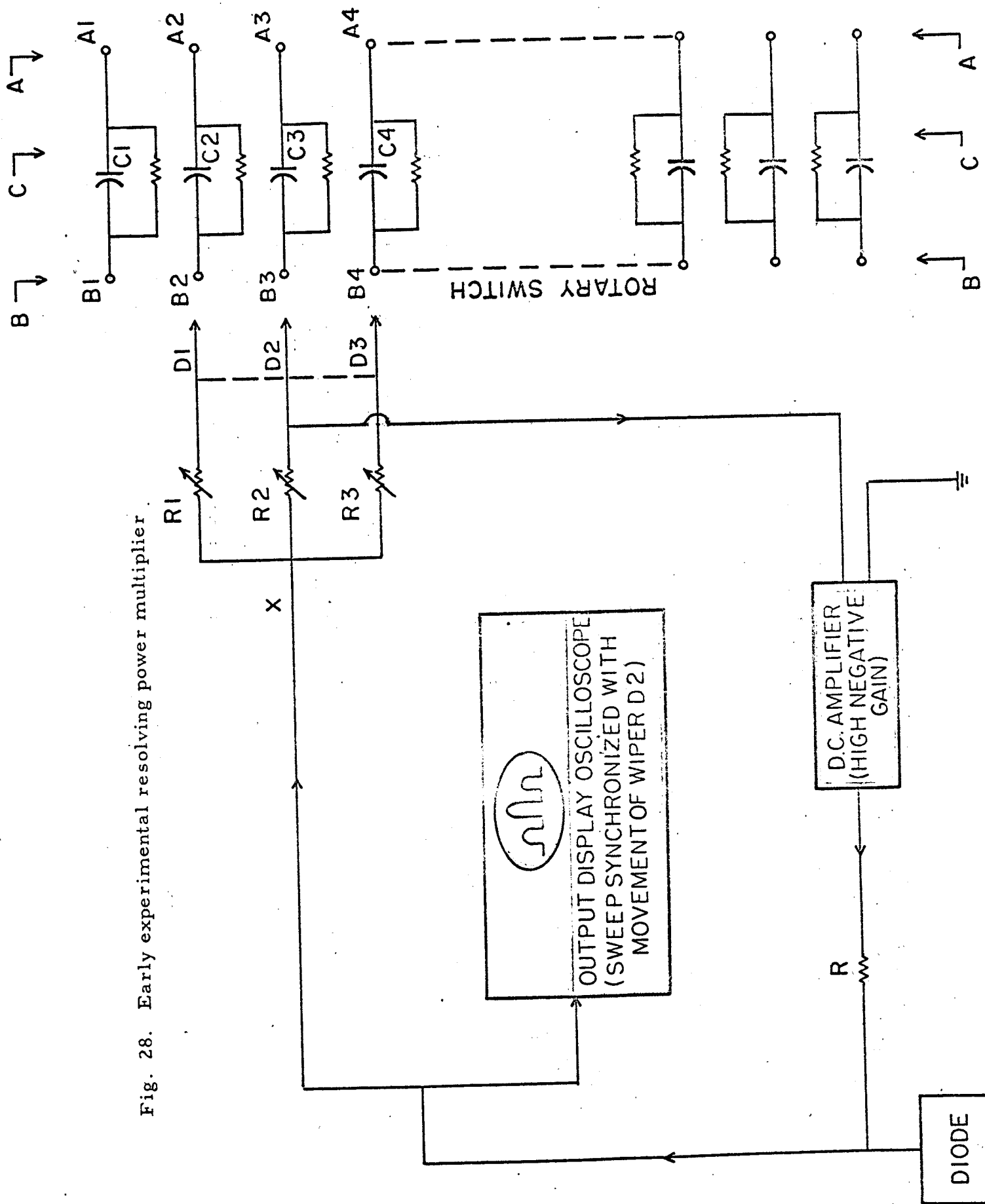
Fig. 27. Block diagram of Resolving Power Multiplier

Fig. 28. Early experimental resolving power multiplier.

terminals and ground. These voltages are respectively proportional to the ion currents indicated by the mass spectrometer when it is set to the successive mass numbers M, M+1, M+2, $\cdots$. C_1, C_2, C_3, $\cdots$ are identical capacitors having identical resistors connected in parallel. The contacts B_1, B_2, B_3, $\cdots$ are the fixed contacts of a rotary switch having multiple wipers D_1, D_2, D_3, which are one contact interval out of phase with each other.

The error voltage between the center wiper D_2 and ground is amplified by the high-gain dc amplifier which then restores D_2 to ground potential by feeding a charge Q into the capacitor to which D_2 is momentarily connected. At the same time, charges QR_2/R_1 and QR_2/R_3 pass through D_1 and D_3 into the capacitors to which they are momentarily connected. R_1, R_2, and R_3 are preset so that they supply a charge pattern which is identical with the ion current pattern in the mass spectrometer for ions having a single mass. The wipers are rotated continuously at a steady rate, the period of which is short compared with the time constant of the capacitors and their parallel resistors. A synchronized oscilloscope trace displays the fluctuations in potential at the point X.

In Fig. 28, the contacts B correspond to ion collectors positioned at successive mass numbers. The current pulses passing through R_1, R_2, and R_3 correspond to the ion currents of a single mass falling on adjacent collectors because of incomplete resolution in the real instrument. The amplitudes of the current pulses at point X correspond to the total currents of ions with mass numbers appropriate to the successive positions of the center wiper D_2. It is these current pulses which represent the relative abundances of the various nuclides in the mass spectrometer.

In a real mass spectrometer, the ions reaching the collector all have charges of the same sign. The analog instrument is therefore prevented from generating signals corresponding to ion currents of negative sign by means of the diode and associated resistor R. The system is unstable without this feature.

The action of the analog circuit is to bring the contacts B essentially to ground potential by a process of successive approximations. Under these conditions, the potentials across the capacitors C and their associated resistors must be equal and opposite to the potentials on the contacts A. Thus, the analog spectrum is identical with the mass spectrometer spectrum at all points corresponding to integral mass numbers. The capacitors tend to discharge slowly through their parallel resistors, the discharge currents being proportional to the potentials on the contacts A. The capacitors are continually recharged by the currents fed through the wiper contacts D.

Because the contacts B and hence the wipers are always close to ground potential, the instantaneous potential at X is proportional to the total instantaneous current to the wipers at that point. This current is, as explained above, representative of the amplitude of the corresponding fully-resolved ion beam. It follows that the instantaneous voltage at the point X can be used as an indication of the relative abundance of the corresponding nuclide in the mass spectrometer. The oscilloscope display, therefore, gives the mass spectrum essentially as it would be displayed by a mass spectrometer capable of completely resolving adjacent peaks.

In practice, five, seven, or more wipers and variable resistors may be required for adequate reproduction of the ion current pattern of ions of a given mass number in the real instrument. An ion current pattern simulated by currents passing through n wipers may correspond to a mass peak up to n+ 1 units wide at its base. A system having n wipers can therefore be used to give resolving-power multiplication factors up to n+ 1.

Several different rotary switch systems have been used successfully. Motor-driven switches operating at up to 200 rpm have been found useful where rapid changes in the real spectrum must be followed. For most other work, however, rotary stepping switches driven at a constant but slower rate have been found to give better

results. Their accurate construction, long life, and reproducible contact characteristics allow considerably more accurate peak height indications to be obtained than is the case with most motor-driven switches.

b. Operating Techniques

If resistors $R_1 \cdots R_n$ have not been adjusted to match the ion current pattern of the real mass spectrometer, the shape of a single mass peak is determined from a calibration run in which a substance giving an isolated peak in the appropriate spectral range is fed into the mass spectrometer. Potentials corresponding to the ordinates of the single mass peak are then applied to terminals A-A. The multiplier is switched on and the amplifier zero setting is checked. Adjustments of the wiper resistors are made until the display shows a single peak at the correct position, and of the correct amplitude (if the amplitude scale has been calibrated). An example of such a display is given on the right of Fig. 29.

To solve a complex peak, potentials representing the ordinates of the complex spectrum, measured at each mass number, are then applied to A-A. Under normal conditions the oscilloscope display then provides the fully-resolved spectrum after completing the 5 to 10 sweeps necessary to reach a steady state.

c. Results

A number of spectra obtained with experimental resolving-power multipliers have been given in previous publications (1, 2).

The spectra given in this paper were all obtained using a simple time-of-flight mass spectrometer operating in conjunction with a more elaborate version of the multiplier described in an earlier section. Results obtained with the simpler unit are very similar except for the somewhat lower accuracy and a more restricted range of resolving-power multiplication factors.

With pure Kr^{86} fed into the mass spectrometer, the mass spectrum shown on the left in Fig. 30 was obtained. The basewidth at 1% of peak height is about 6
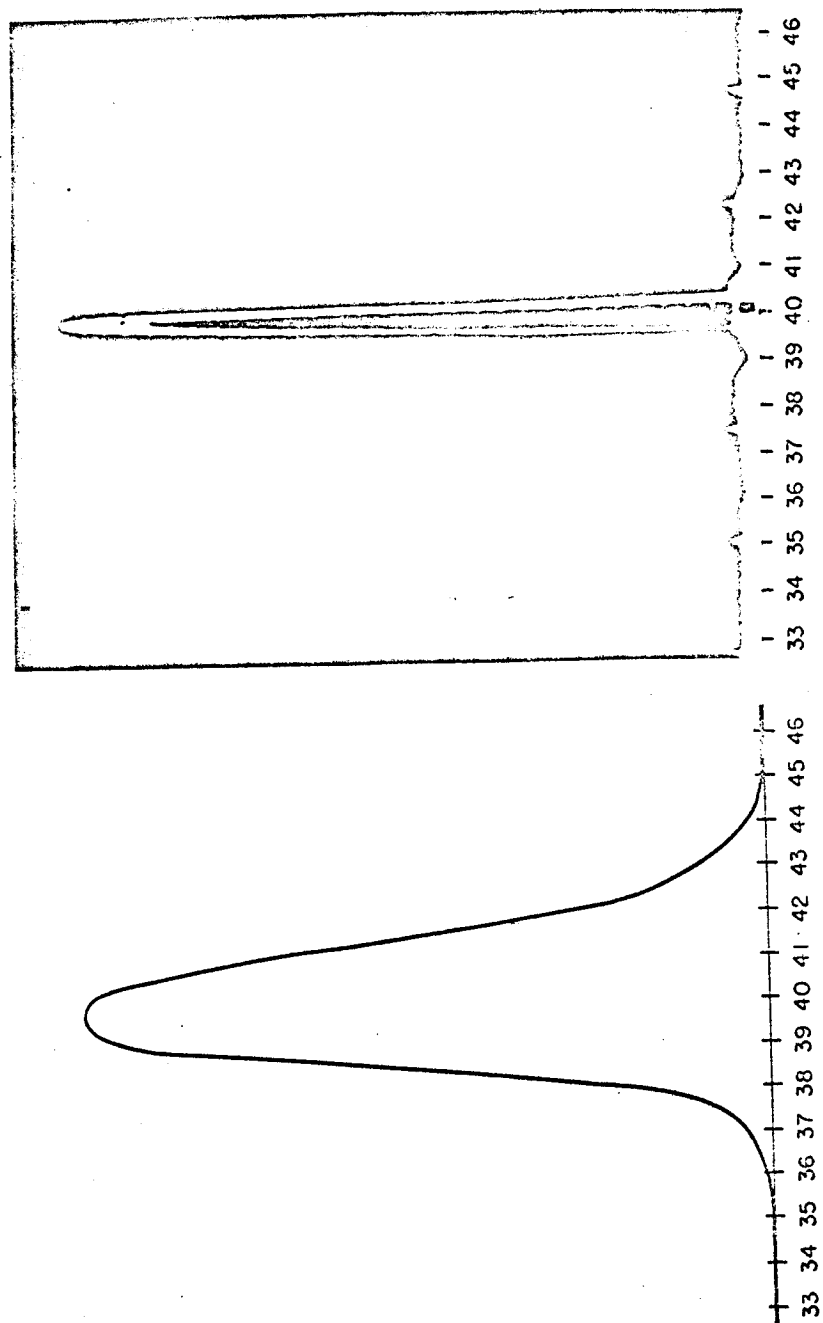
Fig. 29. Sample Gas : Argon 40. (left) Output of mass spectrometer
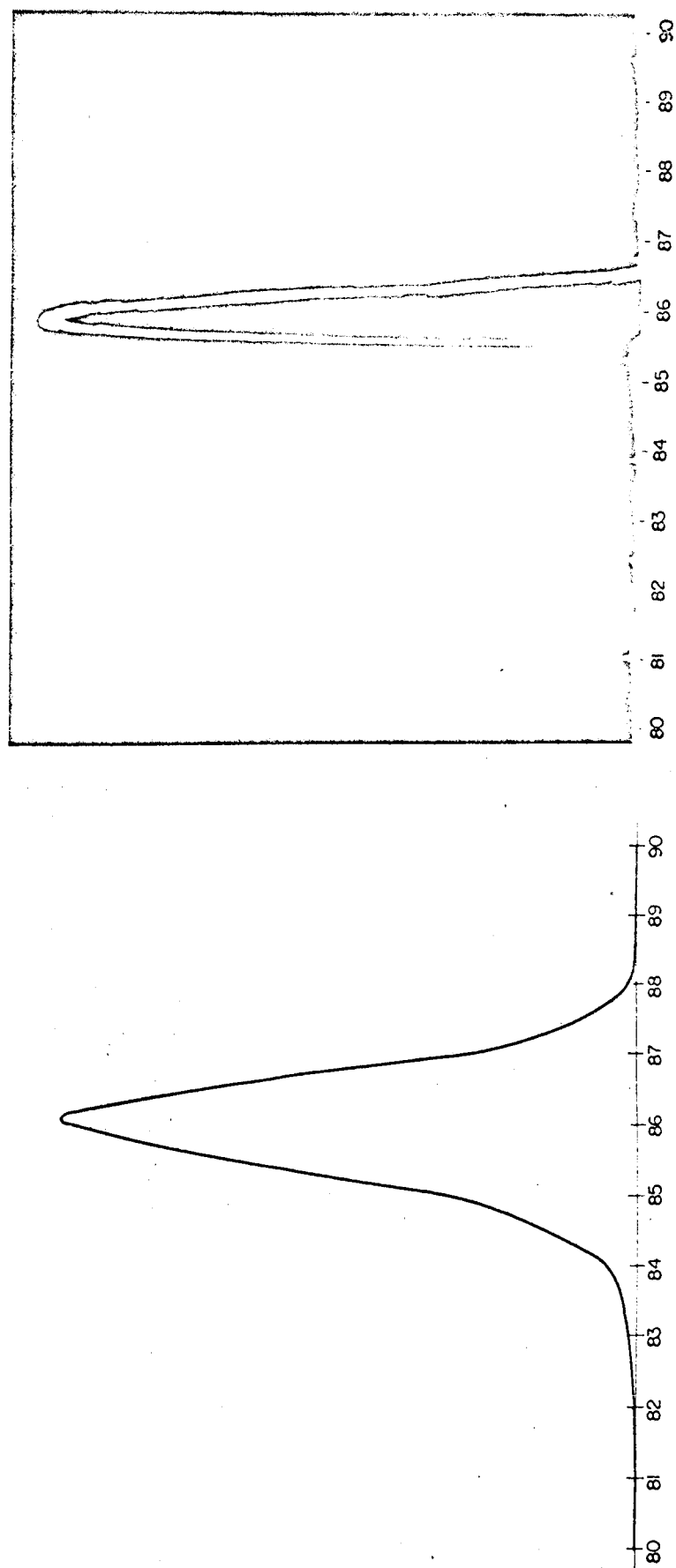(right) Output display of resolving power multiplier

Fig. 30. Sample gas: Kr^{86}. Left: Mass spectrometer output spectrum.
Right: Corresponding multiplier display.

mass units, indicating a resolving power of about 14. A plug-in unit, with poten-
tiometers set to pick off voltages proportional to the ordinate of this peak at each
mass number, was then inserted in the multiplier for a check on the adjustment of
resistors $R_1 \cdots R_7$. The spectrum appearing on the oscilloscope screen is shown
on the right in Fig. 30.

The Kr^{86} was pumped away and normal krypton fed into the mass spectrometer.
A similar procedure was followed. The unresolved and fully resolved spectra are
shown on the left and right, respectively, of Fig. 31. The inset at the right of Fig. 31
shows the normal krypton spectrum as it would appear at the output of an instru-
ment giving triangular mass peaks and having a resolving power of 85. The relative
peak heights are taken from the tables of Bainbridge and Nier (3). The mean error
in the peak heights indicated by the resolving-power multiplier is less than 1% of
the amplitude of the mass 84 peak.

The resolution of the mass spectrometer was then intentionally reduced until
pure Kr^{86} gave an asymmetrical peak more than 9 mass units wide at 1% of its
height. Accurate simulation of such a peak would require 9 wipers and wiper resis-
tors. In this case, an approximate solution was attempted using the 7 available
wipers. The resistors $R_1 \cdots R_7$ were readjusted to match the new peak shape as
closely as possible, and the Kr^{86} was then pumped away. Normal krypton was fed
into the mass spectrometer, giving the spectrum shown on the left of Fig. 32. With
a suitably adjusted plug-in unit in the multiplier, the fully resolved spectrum was
as shown on the right in Fig. 32. The true relative isotopic abundances are again
shown for comparison. In this case, the resolved peak heights are naturally some-
what less accurate than in the previous experiment, although all of the main features
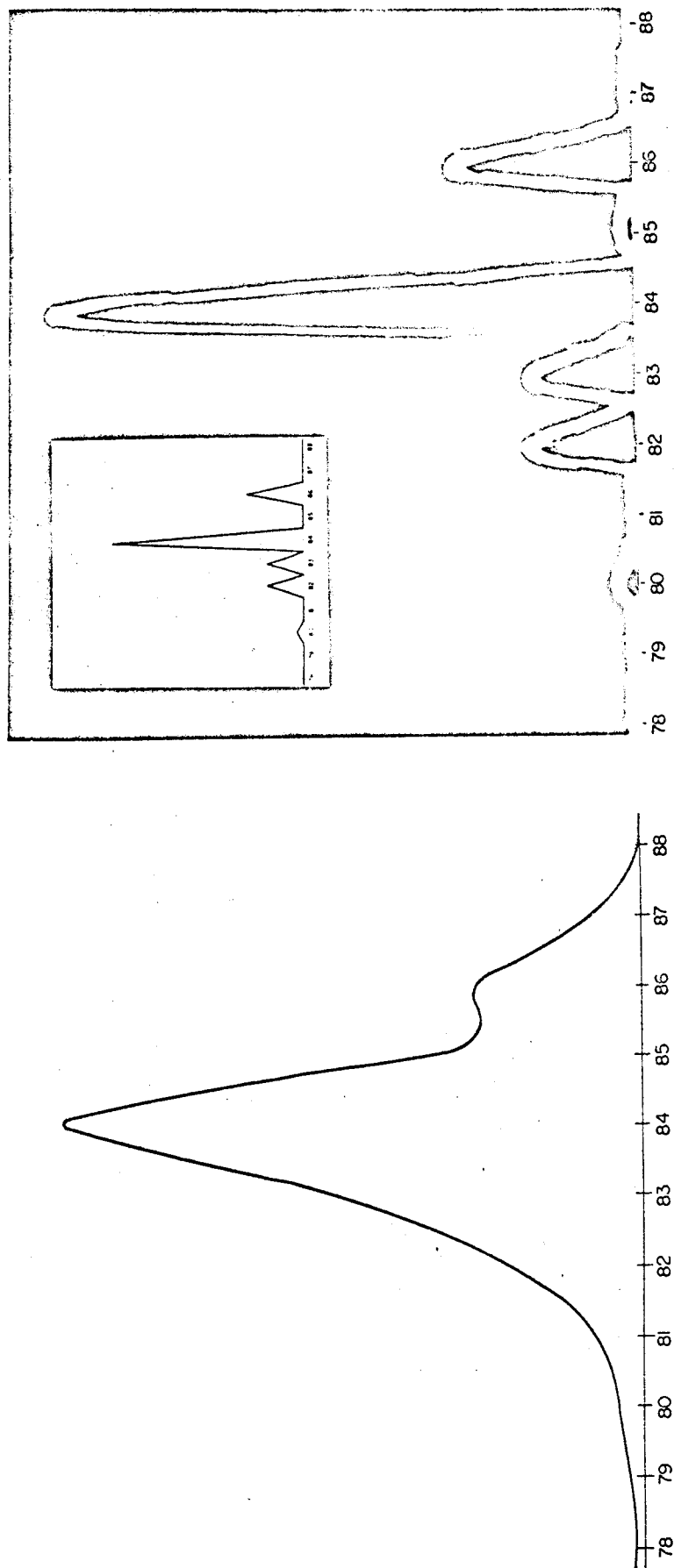of the true spectrum are preserved.

Fig. 31. Sample gas: normal krypton. (left) Mass spectrometer output spectrum. (right) Corresponding multiplier display. (inset) True relative isotopic abundances in normal krypton.
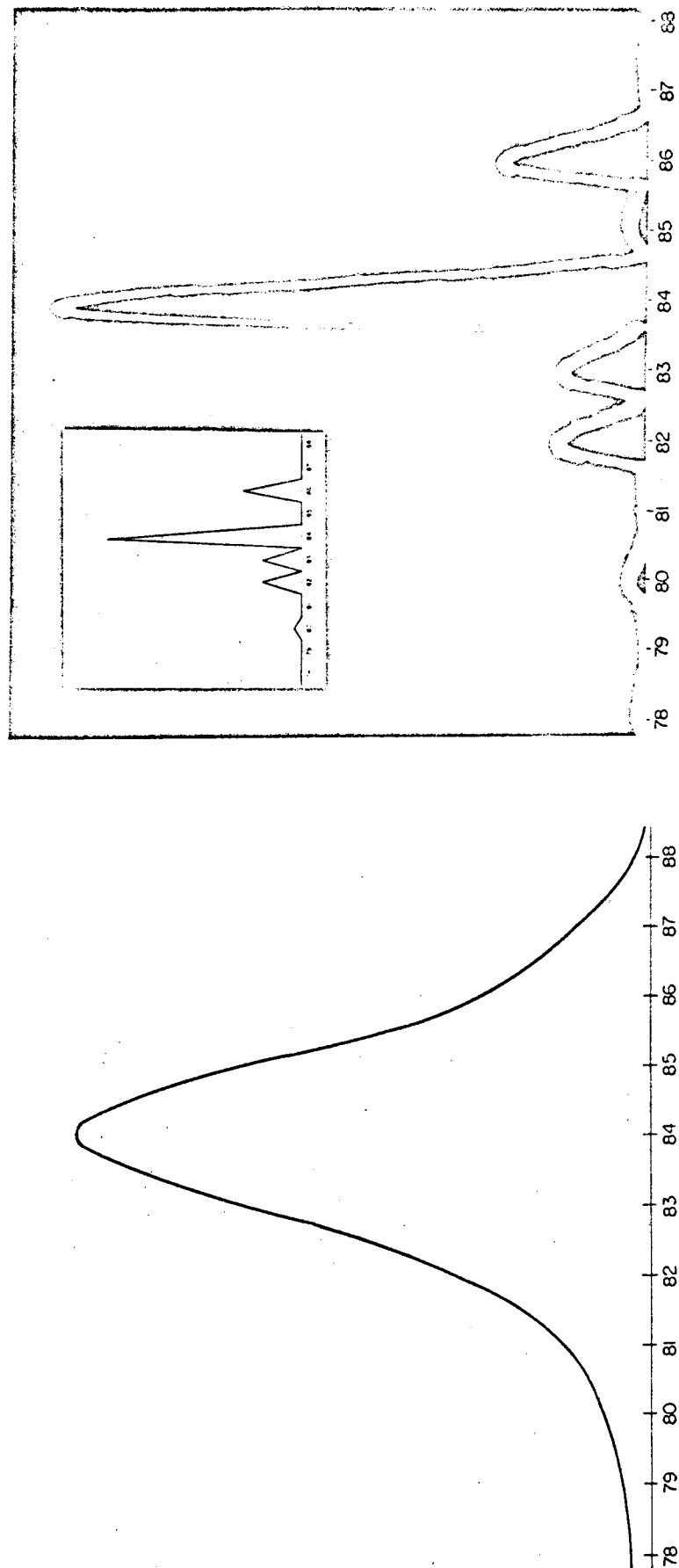
Fig. 32. Sample gas: normal krypton. (left) Mass spectrometer output spectrum at reduced resolving power. (right) Corresponding multiplier display. (inset) True relative isotopic abundances in normal krypton.

d. Applications to Lunar Analyzer

For use in conjunction with a lunar mass spectrometer, the resolving power multiplier has the following important features:

1. It enables a considerable improvement in effective resolving power to be obtained without a corresponding increase in analyzer complexity.

2. It can be operated on the ground, so that there is no weight or power consumption penalty.

3. It can be used to correct for minor analyzer misalignment or damage - provided, of course, that the analyzer is not put out of action completely, and provided that suitable calibration samples are available.

It is strongly recommended that further development of the resolving power multiplier be carried out, and that such a system be considered for use on the ground to analyze telemetered spectra from the lunar mass spectrometer.

3. Calibration Samples

As was pointed out in the introduction to this chapter, there are strong reasons for incorporating into the lunar analyzer a system for introducing calibration samples of known composition. These could be introduced either at preset times or, possibly, on command from the Earth. The calibration samples should definitely include materials likely to be encountered on the Moon, as well as samples of elements covering a wide mass range (preferably isotopically pure) for use in determining the characteristic peak shapes required by the resolving-power multiplier.

REFERENCES

1. Kendall, B. R. F., Rev. Sci. Instrum. 32, 758 (1961).

2. Kendall, B. R. F., Rev. Sci. Instrum. 33, 30 (1962).

3. Bainbridge, K. T. and Nier, A. O. C., Relative Abundance of the Elements, Nuclear Science Series, Preliminary Report No. 9, NRC, USA.

Chapter 8

CONCLUSION

CONCLUSION

The conclusion of this study is that a mass spectrometer with the following characteristics is likely to be the best choice for analyzing samples of the lunar crust and atmosphere:—

    1. Ion source - electron bombardment ionization. Vaporization of solid samples by electron beam or possibly laser beam.

    2. Mass Analyzer - Monopole type.

    3. Ion Detector - electron multiplier, preferably with separate unfocused dynodes.

    4. Internal Calibration - Standard samples of known composition to be analyzed periodically.

    5. Data Processing - Resolving Power Multiplier to be used to process data telemetered from lunar analyzer.

It is assumed that a monopole electrode length of 35 - 65 cm. would be acceptable; the larger figure is obviously to be preferred if space and weight considerations allow it. Such a system should easily be capable of carrying out the mass separations necessary for application of the "normative" technique for mineralogical classification of lunar rocks.

Mass scanning could probably be best accomplished by automatically selecting in turn the masses corresponding to a number of the most important elements associated with the "normative" analysis technique, and then at suitable intervals carrying out mass scans of the complete spectrum in order to detect other elements. If a sufficient number of telemetering channels were available, simultaneous collection and measurement at several of the most important masses would be possible.

In view of the time-of-flight mass analyzer's special advantage of being relatively insensitive to structural distortions, it is worth considering the possibility of using with the monopole analyzer an ion source capable of being pulsed and an ion

detector capable of being momentarily gated on after a variable time interval.
Then, if suitable pulsing circuits could be carried without exceeding weight limita-
tions, a damaged monopole electrode system which was distorted and unusable for
its original purpose could be used as the flight tube for a time-of-flight mass ana-
lyzer operating with the original ion source, ion detector and output system. With
this internal detector-gating arrangement the output circuit does not have to handle
high-frequency signals.

If future changes in mission requirements eliminate the need for the stray
magnetic fields to be kept very small, and especially if the available development
time is short, consideration should be given to using a double-focusing magnetic
mass analyzer instead of the monopole analyzer.

It is suggested that additional research and development should be carried
out in the following areas connected with lunar analysis problems:-

1. Investigation of electron beam vaporization and laser vapori-
zation sources using electron bombardment for ionization. Emphasis
to be placed on miniaturization and reduction of power consumption.
It would also be useful to investigate further the ion sputtering source.

2. Investigation of the characteristics of the Monopole mass analyzer,
particularly as regards resolving power and abundance sensitivity,
for electrode dimensions similar to those for the proposed lunar
instrument.

3. Development of miniaturized memories for use in storing the
results of large numbers of mass sweeps and then telemetering
the results on demand or after predetermined periods of operation.

4. Further development of the Resolving Power Multiplier, with
emphasis on versions not requiring mass scale calibration and
not limited to one peak per mass unit.

5. Preliminary rock analyses which should be carried out in
a terrestrial laboratory to allow satisfactory interpretation of
the lunar data.